A SPECTROSCOPIC STUDY OF SOME SEMIQUINONE RADICAL IONS.

by

Philip James Barker.

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SUMMARY

The effect of substituents on the value of the oxidation potential of quinones is reviewed and attempts to prepare substituted diphenoquinones with high oxidation potentials are reported.

Attempts to characterise the mechanism of addition and substitution in diphenoquinones by identifying the products of the Thiele acetylation of diphenoquinone are reported. The reaction proved most efficient when the incoming acetylinium ion is directed by substituents in the diphenoquinone. A 1,8-addition to diphenoquinone is reported and characterised by isolating the products of the reaction between acetyl chloride and diphenoquinone, with perchloric acid as catalyst.

The alternating linewidth effects observed in e.s.r.spectra are discussed and applied to account for such effects observed in the e.s.r.spectra of diphenosemiquinone anion and cation radicals. The spectra are analysed and the intramolecular processes producing these effects are discussed. A dianion diradical where intramolecular rotation about the 1 - 1' bond is restricted is produced by the oxidation of 2,2',4,4'-tetra hydroxybiphenyl.

Previous studies of diphenosemiquinone anions are reviewed and alkylated diphenosemiquinone anion are produced by the reduction of the parent quinone with potassium hydroxide solution, the resulting radical being stabilised by the presence of pyridine. A qualitative interpretation of the solvention effect in alkylated diphenosemiquinone anions is given.

Diphenosemiquinone cation radicals are reviewed and previous studies are re-examined.

For Brenda -

So far away but

So very near.

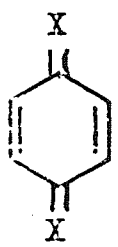
CONTENTS.

CHAPTER ONE.

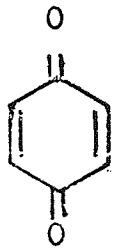
INTRODUCTION.

1. QUINONES.

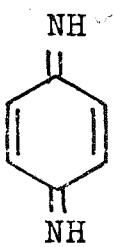
In their most simple form, quinones may be considered as cross-conjugated systems of type I, where the exocyclic group may be heteroatomic as in the cases of quinones and quinone diimines (IIa and IIb respectively), or where the molecule is polyolefinic in nature, as in quinodo-dimethanes (III).



I.



IIa.



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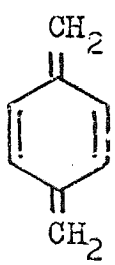
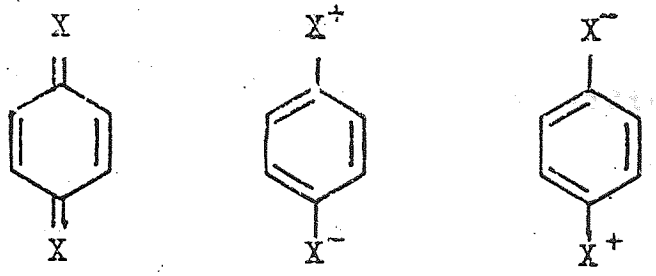


III.

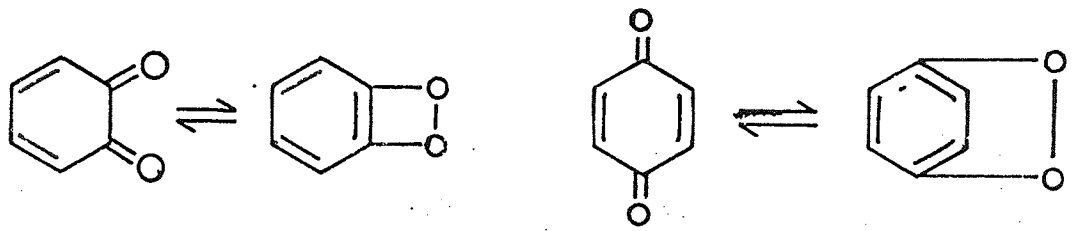
One might expect the chemistry of these compounds to show little difference between their properties and those of of the theoretical treatments derived for cross-conjugated olefins (1) or conjugated ketones (2), which should be applicable here. There is however, a direct relationship between the quinonoid and benzenoid functionalities which may be illustrated by the resonance structures in figure 1.a.



etc.

1.a.

Prior to this resonance approach was the concept that equilibrium might exist between quinones and cyclic aromatic peroxide structures as in figure 1.b.(4,5).



1.b.

Although there is little to make this idea feasible, even aware of more modern evidence, it may serve to illustrate the relationship between quinonoid and benzenoid structures that was apparent to earlier workers. This relationship and the theoretical aspects of the structure and aromaticity of quinones are described more fully elsewhere (6,7), but these three considerations each contribute to the many and varied aspects of quinone chemistry.

2. Oxidising Properties of Quinones.

Quinones have been known as oxidising and dehydrogenating agents since the late 19th Century. In the dehydrogenation of aromatic hydrazo compounds, Dimroth (8) made the first attempts to relate the rate of dehydrogenation with the oxidation potential (E_o) of the quinone used for the reaction and found that the nature of the substituents in the quinone greatly affected the rate of reaction. Similar experiments were repeated on other quinone dehydrogenation and oxidation reactions and since Dimroth's early work, much information on the kinetics and mechanism of such reactions has been obtained and oxidation potentials of large numbers of quinones have been measured, data having been summarised by Clarke (9). Quinones with high oxidation potentials are now well established as reagents in organic synthesis (-10). The oxidation potentials of some substituted 1,4-benzoquinones are summarised in table I. In general, it can be seen that alkyl, alkoxy and most electron donating groups tend to decrease the oxidation potential (relative to unsubstituted 1,4-benzoquinone), while halogens, the cyano- group and electron withdrawing groups (acetyl, nitro- etc.) increase E_o. In recent years, the uses of quinones as oxidants have branched into many spheres of organic, organometallic, polymer and inorganic chemistry (11). The quinones most commonly used in organic synthesis are 1,4-benzoquinone, chloranil (tetra-chloro-1,4-benzoquinone), and 2,3-dichloro-5,6,-dicyano-1,4-benzoquinone (DDQ).

1,4-Benzoquinone	E_o (mV)	Ref.
2,3-Dichloro-5,6-dicyano-	1000	11
2,3-Dicyano-	971	9
2,5-Dibromo-	768	9
Tribromo-	763	9
Trichloro-	755	9
Tetrachloro- (Chloranil)	742	9
2,6-Dichloro-	740	9
Iodo-	737	9
Methyl-	645	11
2,6-Dimethyl-	593	11
Trimethyl-	527	11
2,6-Di-tert-butyl-	496	11
Tetramethyl-	463	11

Table I. The oxidation potentials of some 1,4-benzoquinones(reference is unsubstituted benzoquinone, E_o= 711mV.).

4,4'-Diphenoquinone	E_o	Ref.
3,3',5,5'-Tetrachloro-	1100	11
Unsubstituted	954	13
3,3',5,5'-Tetramethyl-	845	13
3,3',5,5'-Tetraisopropyl-	735	13
3,3',5,5'-Tetra-sec-butyl-	685	13
3,3',5,5'-Tetra-tert-butyl-	675	13

Table II. Oxidation potentials of some 4,4'-diphenoquinones(ref.1,4-benzoquinone,E_o= 711mV).

DDQ was first prepared by Wallenfels et Al.(12) and, having the highest oxidation potential of all stable quinones has found wide application. The high oxidation potential quinone tetracyano-1,4-benzoquinone has been prepared (11), but due to its high reactivity and moisture sensitivity (both cuased by the high E_o), its anticipated application has not been fulfilled.

The oxidation potentials of several substituted diphenoquinones have been measured (13), and are summarised in table II.

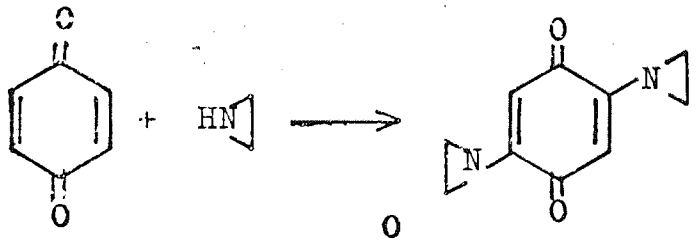
From a comparison of tables I and II it can be seen that 3,3¦5,5'-tetra-substituted diphenoquinones have considerably higher oxidation potentials than their correspondingly substituted 1,4-benzoquinone analogues. Surprisingly, no attempts to prepare cyano- and mixed halogen-and cyano substituted diphenoquinones, which may have extremely high oxidation potentials and thus widespread application in organic synthesis, have been reported.

3. Quinones with Nitrogen Containing Substituents.

The substitution of the ring protons in 1,4-quinones by nitrogen containing groups (amino-, dialkylamino-, imines azides etc.) has been a major area of study in quinone chemistry. Such compounds, and particularly those where the nitrogen atom is bonded to the quinone ring, have found extensive use in research in life-systems. Many general

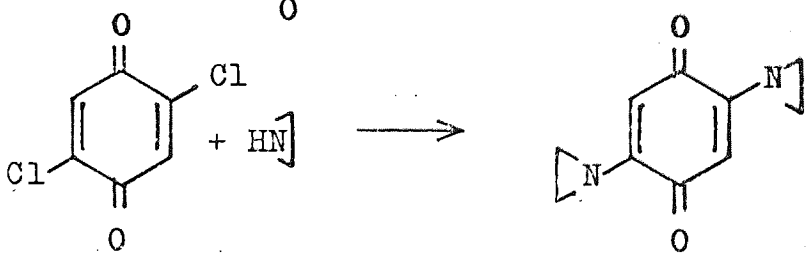
methods of preparaion are found in a paper by Silver and Holmes (14), dealing with the use of substituted 1,4-naptho-quinones as bacterial growth inhibitors. Many potentially useful drugs have been synthesised (15, 16, 17), and the characterisations of many natural products containing a wide range of substituted quinones have been reported (15).

1,4-benzoquinones and hydroquinones containing ethylenimino substituents have been found to be effective cytostatic agents and this observation has led to a great deal of synthetic research in this area (18, 19). As with other imines, normal Michael addition is a useful route to some derivatives, while in some examples, substitution reactions are the preferred route.

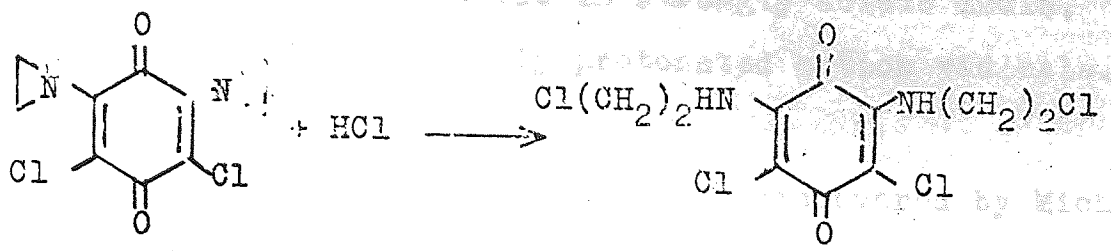


1.i.

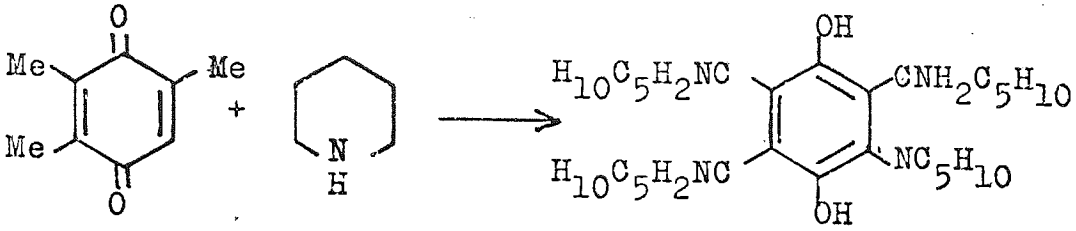
1.ii



In quinones containing ethylenimino groups or piperidino substituents, ring opening is easily achieved to yield a route to many new aminated products. In the case of the addition of piperidine to trimethyl-1,4-benzoquinone, both substitution and side-chain amination takes place, as in equations 1.iii and 1.iv below,



1.iii.



1.iv.

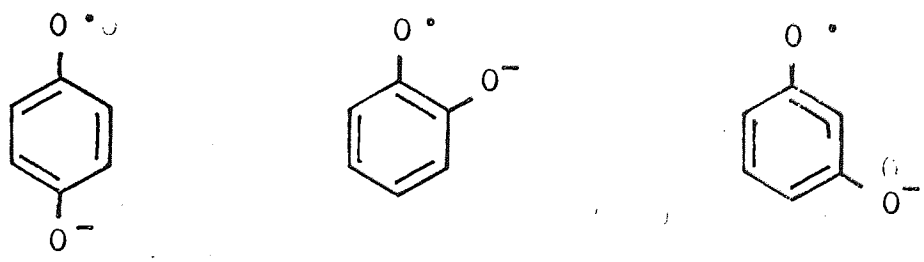
In addition to the examples mentioned, the kinetics and mechanisms of substitution by amino and related groups of large numbers of quinones are now known (although none have been reported for diphenoquinones) and have been well reviewed by Finlay (20).

4. Semiquinones.

The reduction of quinones to dihydroquinones (referred to as hydroquinones) is a reversible process involving the addition of two electrons and two protons. These electrons may be transferred from suitable electron donors singly, producing intermediates whose oxidation state lies half way between that of the quinone and that of the hydroquinone. These intermediate species are termed semiquinones. The exact nature and stability of these semiquinones is dependent to a major degree on the pH of the reaction medium. In alkaline media, semiquinones exist as anion free-radicals which gain extra stability from increased delocalisation of the unpaired electron, while in strongly acidic media,

the unpaired electron, while in strongly acidic media, semiquinones exist as doubly protonated cation radicals.

Semiquinone anion radicals were first discovered by Michaelis (21) in 1931, his subsequent studies (22) establishing their nature and factors determining the various equilibria in solution. With the advent of electron spin resonance (e.s.r.) spectroscopy, the examination of semiquinones became one of the first major areas of study using this technique (23). 1,4-semiquinones have been extensively studied by e.s.r. in order to determine the role and effect of substituents upon the π-electron distribution in the system and their study has been facilitated by the fact that they are stable in a variety of redox media. On the other hand, 1,2-semiquinones have been found to be much less stable and prone to forming secondary radicals (24). Although 1,3-quinones do not exist, e.s.r.spectra of 1,3-semiquinone radicals have been produced by the oxidation of the corresponding 1,3-dihydroxybenzenes (24).



Semiquinone cation radicals were first detected by Land and Porter using u.v.spectroscopic techniques (25). Electron spin resonance studies on these radicals were subsequently

carried out in concentrated sulphuric acid solution by Bolton and Carrington (26). A feature of the study of semiquinone cation radicals has been the observation of hydroxyl proton splittings, variations in spectral linewidth have been observed depending on whether the two hydroxyl groups are orientated cis- or trans- with respect to each other (27), much information about inter- and intramolecular processes can be gained from the study of such linewidth variations (28) and this is fully described in later chapters.

Although semiquinone anions and cations have been those semiquinones most studied, intermediate quinones have been observed. The monoprotonated species of semiquinone radical exists only in neutral or weakly acidic media is very unstable and disproportionates into the parent quinone and hydroquinone. Charge-transfer complexes are also formed between the monoprotonated semiquinone (as electron donor) and the quinone (as electron acceptor), these adducts, quinhydrones are crystalline materials, insoluble in aqueous media with complex crystal structures and chemistry (29).

Neutral semiquinones remained undiscovered until ten years ago when they were prepared photolytically and detected in weak acid solution using an e.s.r.fast flow technique(30).

For the 1,4-benzoquinone- hydroquinone system, a summary of the relationships between the parent compounds and the semiquinone intermediates is given in figure 1.d.

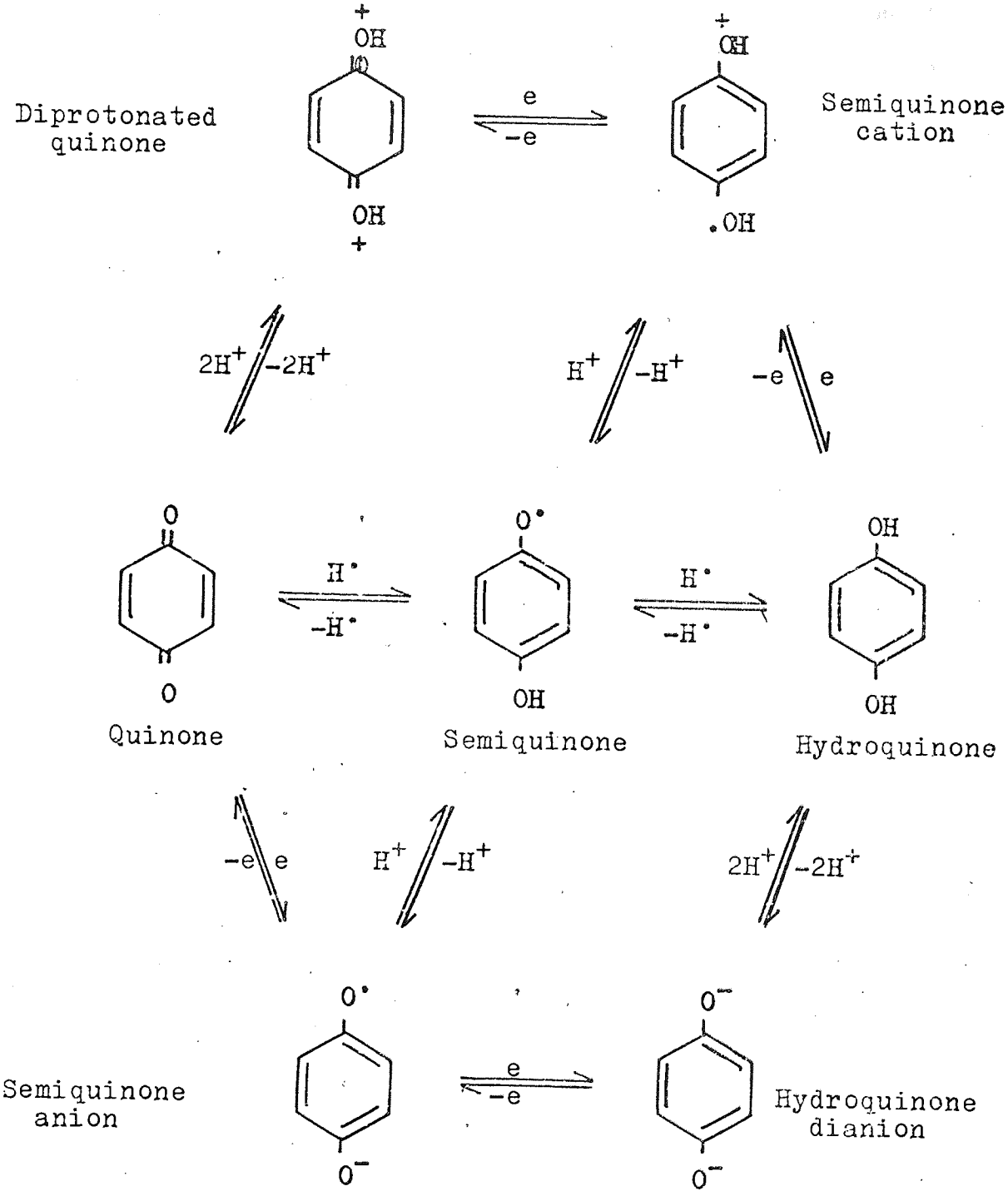
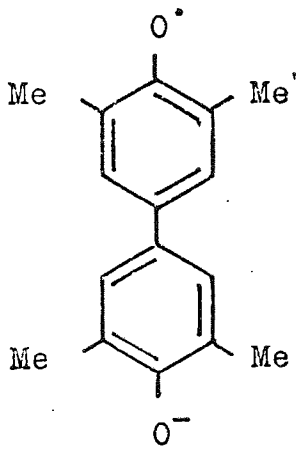

Diprotonated quinone
e
-e
Semiquinone cation
2H+
-2H+
H+
-H+
-e
e
H·
-H·
Quinone
Semiquinone
Hydroquinone
Semiquinone anion
Hydroquinone dianion

figure 1.d.

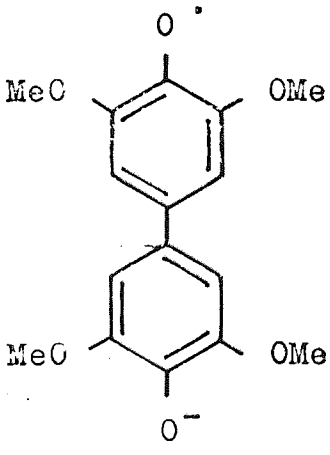
5. Diphenoquinones.

Until the present time, the majority of the research in semiquinone chemistry has been carried out upon 1,4-benzosemiquinones and their 1,4-naptho- and 9,10-anthrasemiquinone analogues. Comparitively little research has been carried out on diphenosemiquinones, and its related compounds.

Matsunaga and MacDowell (31) reported the e.s.r.spectra of the 3,3¦5,5'-tetramethyl- and 3,3¦5,5'-tetramethoxydiphenosemiquinone anions (V & VI), prepared by the air oxidation of the corresponding biphenyl-4,4'-diols.



V



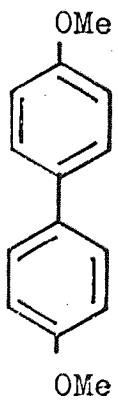
VI

Matsunaga subsequently published a further paper giving alternative assignments for the hyperfine coupling constants of the tetramethyl derivative (32). These radicals were produced in a solvent mixture of aqueous (2M) potassium hydroxide solution and pyridine in a 1 : 1 ratio, and it has been shown (33) that varying the mole fractions of these solvents changes the hyperfine splittings of both sets of protons in the tetramethyldiphenoquinone anion. These changes

were shown to be due to the solvation of the anions by the hydroxylic solvent molecules, hydrogen bonded to the carbonyl oxygen atoms.

Forbes and Sullivan (34) noted that oxidation of biphenyl-4,4'-diol by a mixture of aluminium chloride and nitromethane yielded a paramagnetic blue solution. The resulting e.s.r. spectrum was analysed in terms of two groups of four equivalent protons and one group of two. It has now been ascertained that the e.s.r.spectrum of biphenyl-4,4'-diol dissolved in concentrated sulphuric acid containing a trace of oxidising agent shows seventeen equidistant lines which arises from two groups of four equivalent protons, there being no hydroxyl proton interaction (33).

Cation radicals derived from 4,4'-dialkoxybiphenyls have been reprted by Sullivan (35), and for the dimethoxybiphenyl cation the magnitude of the proton hyperfine splittings followed the ratio $a^{H}_{2,6} > a^{H}_{CH_3} > a^{H}_{3,5}$.

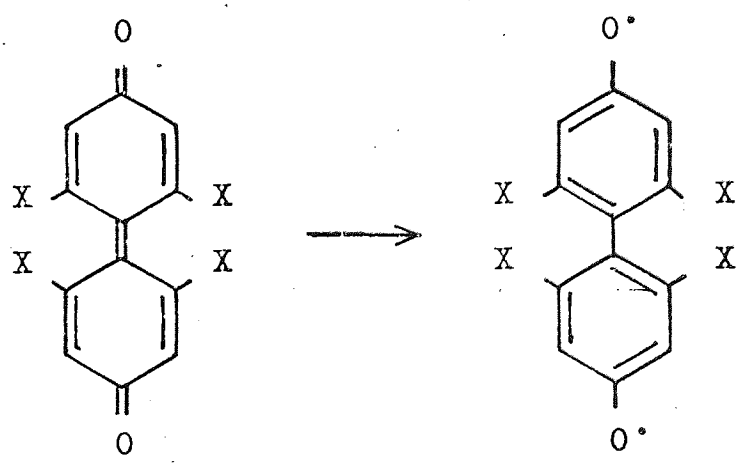


Cation radicals derived from these compounds may be termed

as 'violenes', after Hünig (36) in that they have, in the delocalised π-system 2n + 3 π-electrons shared by 2n + 2 atoms (37).

Anion radicals of alkylated diphenoquinones have been produced by chemical and electrochemical methods (33, 38) and their e.s.r.spectra and the spectra of secondary radicals derived from them have been identified.

It has been reported that in radicals produced from diphenoquinones and 4,4'-dialkoxybiphenyls, it may be possible to observe restricted rotation effects about the 1 - 1' carbon-carbon bond.(28). It has also been suggested that if hindered quinones of type VII, could be produced and rotation about the 1 - 1' bond was sufficiently restricted or even fixed and thus there was no interaction across the 1 - 1' bond by the unpaired electron, then diradicals may be produced (39).



VII VIII

6. Present Work.

The aims of the present work are ;

To prepare new derivatives of diphenoquinones, in particular those substituted with groups that may increase the value of the oxidation potential from that of unsubstituted diphenoquinone (954mV) especially cyano- groups. In general to characterise the mechanisms of addition and substitution in diphenoquinones.

To study the diphenoquinone anion and cation semiquinone free radicals,using e.s.r.spectroscopy,that exhibit alternating linewidths in their spectra. To analyse these spectra and characterise the inter- or intramolecular processes responsible for them.

To reexamine previous studies of alkylated diphenosemiquinone anion and cation free radicals, noting any discrepencies in the results and making clear any ambiguity arising from comparisons of these results.

CHAPTER TWO.

EXPERIMENTAL WORK.

A. Preparation of Compounds.

1. Biphenyl-4,4'-diol.

A commercial sample of this compound was obtained from the Aldrich Chemical Co. Ltd. It was recrystallised from glacial acetic acid, yielding white, crystalline platelets melting at 279-280°C, literature value 280-283°C (40).

Analysis : Calculated for $C_{12}H_{10}O_2$, C : 77.43%, H : 5.39%,

found, C : 76.80%, H : 6.40%.

2. 4,4'-Diphenoquinone.

4,4'-Diphenoquinone was prepared by the method of König et Al.(41). A solution of 2.0g biphenyl-4,4'-diol in 80cm^3 of dry 1,4-dioxan was added slowly, with stirring, over a period of five minutes to a solution of 7.14g of lead (IV) acetate dissolved in 140cm^3 of glacial acetic acid. The clear red solution was stirred for a further five minutes, while the temperature was maintained at 35°C, and then cooled in an ice-bath. The resulting red needle-like crystals were filtered, washed twice with glacial acetic acid and then 60°-80°boiling petroleum ether, and recrystallisation from glacial acetic acid gave 1.5g dark red needles, m.p.160°C with decomposition, lit.val. 160°-165°(decomp.)(2).

Analysis : Calculated for $C_{12}H_8O_2$, C : 78.27%, H : 4.33%,
found, C : 79.80%, H : 4.12%.

FOOTNOTE.

Although a seemingly straightforward preparation, it is often hampered by the formation of complex further oxidation and addition products. The mechanism of the oxidation of phenolic compounds by lead(IV)acetate is not fully understood, but it is believed that firstly, addition products involving the phenolic oxygen atoms and lead triacetoxy species are formed (42) and this is followed by successive substitutions about the benzene rings (see figure 2.a.).

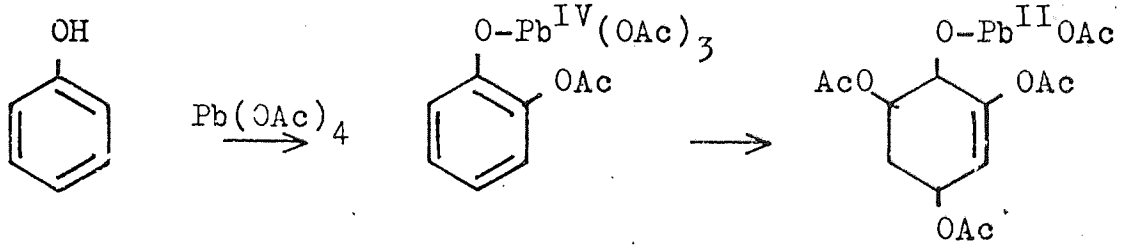


fig.2.a.

If the temperature of the reaction medium is not strictly controlled during the addition of the biphenyl-4,4'-diol solution (which must be effected with extreme caution), then copious amounts of addition products are formed and no diphenoquinone.

3. 3,3',5,5'-Tetrabromobiphenyl-4,4'-diol.

The method of Magatti (43) was used in the preparation of this compound. 2g of biphenyl-4,4'-diol were dissolved in the minimum quantity of hot glacial acetic acid. Bromine was then added dropwise, with stirring, until the red colouration did not disappear. On cooling, a white solid separated which was filtered, washed twice with acetic acid, then recrystallised from absolute ethanol to give fine, white needles m.p.268°C, lit.val.267°C(4).

Analysis : Calculated for $C_{12}H_6Br_4O_2$, C : 28.68%, H : 1.19%,
found, C : 29.50%, H : 1.31%.

4. 3,3'-Dimethylbiphenyl-4,4'-diol.

This compound was prepared from 3,3'-dimethylbenzidine, by a modified Sandmeyer synthesis (44). 11.1g of the benzidine were dissolved in 500cm^3 of water containing 29.2cm^3 of concentrated hydrochloric acid, the whole being cooled to 5°C. A cold solution of 7.25g of sodium nitrite in 40cm^3 water was then added slowly, keeping the temperature below 5°C, until an excess of nitrous acid was present. The diazotised solution was divided into five equal parts. Each part was boiled for ten minutes with 180cm^3 of water containing 20cm^3 phosphoric(V)acid. On cooling, each of the five parts were extracted with ether and trituration of the combined extracts with benzene yielded a pale yellow crystalline solid. Recrystallisation from aqueous ethanol gave very pale yellow crystals, m.p.165°C, lit.val.162-164°C (44).

Analysis : Calculated for $C_{14}H_{14}O_2$, C : 78.5%, H : 6.54%,
found, C : 78.33%, H : 6.50%.

5. 4,4'-Dimethoxybiphenyl.

Dimethyl sulphate has long been recognised to be an excellent alkylating agent for phenolic hydroxyl groups (45), the reaction being both efficient and convenient. This method was used therefore, in preference to the more elaborate process involving the use of methyl iodide and sodium carbonate (46). 2g of biphenyl-4,4'-diol were dissolved in 50cm^3 of 2M potassium hydroxide solution. The calculated volume of dimethyl sulphate was added and the flask was tightly stoppered. The system was stirred for one hour, magnetically. After this period a white suspension had formed, this fine suspension was filtered and recrystallised from methanol to yield white crystals, m.p.171 °C, lit.val.173°C.

Analysis : Calculated for $C_{14}H_{14}O_2$, C : 78.50%, H : 6.54%,
found, C : 79.60%, H : 6.35%.

FOOTNOTE.

Extreme caution must be exercised when using dimethyl sulphate in this preparation. Although not particularly volatile it is absorbed easily through the skin. The toxicity of dimethyl sulphate may be illustrated by a comparison of threshold limit values (the threshold limit value is the maximum permitted level of a substance in parts per million in the atmosphere in a working or inhabited environment)

the t.l.v. of HCN is 10p.p.m., that of elemental bromine (vapour) is 0.01p.p.m. while that of dimethyl sulphate is 0.001p.p.m.

6. 3,3',5,5'-Tetrabromo-4,4'-dimethoxybiphenyl.

This compound was prepared by a similar method to that above, using 3,3',5,5'tetrabromobiphenyl-4,4'-diol as starting material. After recrystallisation from methanol, a white crystalline solid was obtained,m.p. 184°C, lit.val.185°-186°C (47).

Analysis : Calculated for $C_{14}H_{10}Br_4O_2$, C : 39.16%, H : 1.85%,
found, C : 38.75%, H : 1.80%.

7. 4,4'-Diethoxybiphenyl.

Again a similar method to that used for the dimethyl analogue of this compound was utilised in this preparation. The starting materials were biphenyl-4,4'-diol and diethyl sulphate (2g of diol and 1ml of diethyl sulphate). Upon recystallisation from methanol, white needles of product were isolated m.p.159 °C, lit.val.156 °C (8).

Analysis : Calculated for $C_{16}H_{18}O_2$, C : 79.33%, H : 7.44%,
found, C : 78.75%, H : 7.60%.

8. 4,4'-Diphenoxybiphenyl.

This compound was synthesised according to the method of Kruglov and Kotlyarevski (48), starting from 4,4'-dibromobiphenyl, which in turn was prepared by the method of Scholl

and Neovius (49) by the addition of bromine to biphenyl.

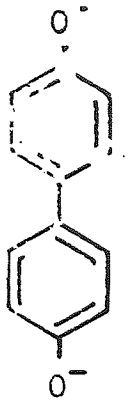
5g of 4,4'-dibromobiphenyl, 8.5g phenol, 7.5g of anhydrous potassium carbonate and 0.2g of copper powder were heated together under reflux , at 240°C, for six hours. After cooling, the resultant solid mass was groun in a mortar and then boiled for one hour with 100cm^{3}of 5% sodium hydroxide solution. The precipitate formed in this process was filtered, washed with alkali, washed again with water and then dried. This solid product was taken up in a solvent mixture of ether and dichloroethane (1 ; 1 by volume), any undissolved material then being removed and discarded. The solution was passed through an alumina column, and on evaporation of the solvent 1.7g of pale yellow crystals were obtained, m.p.150°, lit.val.151°-153°C (48).

Analysis : Calculated for $C_{24}H_{18}O_2$, C : 85.21%, H : 6.71%,
found, C : 84.25%, H : 7.35%.

9. 4,4'-Di-(p-nitrophenoxy)-biphenyl.

In alkaline solution, biphenyl-4,4'-diol exists as the dianion I, while in the same medium, p-chloronitrobenzene might be expected to behave as in II and III.

Nucleophilic attack by the dianion I on the position 4 centre in two separate p-chloronitrobenzene molecules would thus lead to the desired product.

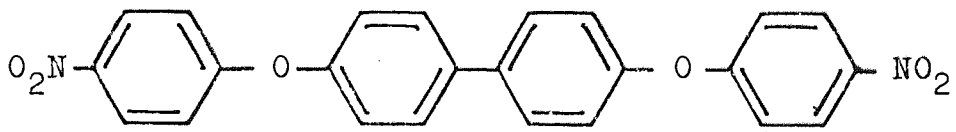


I

II

III

2g of biphenyl-4,4'-diol were dissolved in 100cm^3 of a 2M solution of potassium hydroxide and this solution was magnetically stirred during the addition of 3g of finely ground p-chloronitrobenzene. The flask was tightly stoppered and stirring was continued for a further eight hours. At the end of this time a fine white suspension had formed, this was filtered and recrystallised from methanol to yield product IV.



IV

m.p. 185 °C.

Analysis : Calculated for $C_{24}H_{16}N_2O_6$, C : 67.30%, H : 3.74%, N : 6.54%,

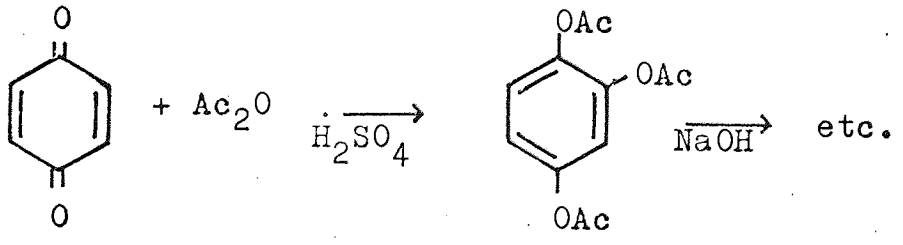
found, C : 66.25%, H : 3.50%, N : 6.22%.

THE ACETYLATION OF DIPHENOQUINONES.

The Thiele acetylation reaction is fully described in chapter three. The general method for the preparations was that of Vogel (46).

1g of the quinone to be acetylated was suspended in $5cm^3$ of acetic anhydride. The reaction vessel was maintained in an ice-water bath at 5^oC or below, and $0.1cm^3$ of concentrated sulphuric acid were cautiously added, the mixture being stirred throughout (N.B. During the reaction the temperature rises rapidly, and has to be kept well below 50^oC to avoid the formation of complex addition products. The reaction is complete when the temperature starts to fall.). The reaction mixture was allowed to stand for fifteen minutes and was then poured into $20cm^3$ of water. The residue, containing the acetylated products, was filtered, dried, and then taken up in 1M sodium hydroxide solution (the actylated products were never isolated but always hydrolised thus, in order to obtain directly the hydroxy- derivatives) and boiled for one hour. Any undissolved material was discarded after filtration, the filtrate being then acidified with dilute hydrochloric acid. The precipitate formed after acidification, containing the hydroxy- derivatives of the acetylated quinones, was isolated and the product, in some cases a mixture of several compounds, was separated and recrystallised.

The reaction, performed on diphenoquinone and some of its alkyl derivatives, is illustrated for 1,4-benzoquinone.



10. 3,3',5,5'-Tetramethylbiphenyl-2,4,4'-triol.

This compound was prepared by the acetylation of 1g of 3,3',5,5'-tetramethyldiphenoquinone using acetic anhydride with concentrated sulphuric acid as catalyst. After the hydrolysis of the acetylated product, the biphenyltriol was recrystallised from benzene to give pale yellow crystals m.p.174°C.

Analysis : Calculated for $C_{16}H_{18}O_3$, C : 74.8%, H : 7.00%
found, C : 72.92%, H : 6.4%.

11. 3,3',5,5'-Tetramethoxybiphenyl-2,4,4'-triol.

12. 3,3',5,5'-Tetra-tert-butylbiphenyl-2,4,4'-triol

These two compounds were prepared by similar methods to that above using the corresponding diphenoquinone as starting material. 11 was recrystallised from benzene to give a white crystalline solid m.p.161°C. 12 yielded a pale coloured solid onrecrystallisation from the same solvent.

Analysis : 11, $C_{16}H_{18}O_7$, calculated C : 55.90%, H : 5.59%,
found, C : 57 .58%, H : 4.83%.
12, no analysis results.

13. 3-Chlorobiphenyl-4,4'-diol.

The general method of acetylation was modified in the preparation of this compound. The Thiele acetylation was found to be unsuccessful when performed on diphenoquinone, but a related reaction involving the use of acetyl chloride as the acetylating agent proved successful.

1g of diphenoquinone was suspended in $5cm^3$ of acetyl chloride and $0.1cm^3$ of concentrated perchloric acid was cautiously added. The reaction mixture was stirred while the whole was immersed in an ice bath. The temperature rose sharply and care was taken to keep it below 50^oC. When the reaction was complete, the mixture was allowed to stand at room temperature for half an hour before being taken up in water and hydrolising, as in the general acatylation method. After hydrolysis with sodium hydroxide and then acidification with dilute hydrochloric acid, a pale yellow crystalline product was isolated. This product was found to be a mixture of two compounds after a simple t.l.c. experiment. It seemed likely that one of these products may be biphenyl -4,4'-diol so the two compounds were separated by fractional crystallisation from glacial acetic acid, and then successively recrystallised until constant melting point was achieved.

0.21g of a white crystalline solid were obtained, m.p.280^oC giving i.r. and analysis results similar to those for biphenyl-4,4'-diol, the e.s.r.spectrum of a little of this compound dissolved in $1cm^3$ of concentrated sulphuric acid

containing a trace of hydrogen peroxide corresponded to that of the diphenosemiquinone cation radical.

The second product, 0.28g of a pale crystalline solid was found to be 3-chlorobiphenyl-4,4'diol .

m.p. 254°C.

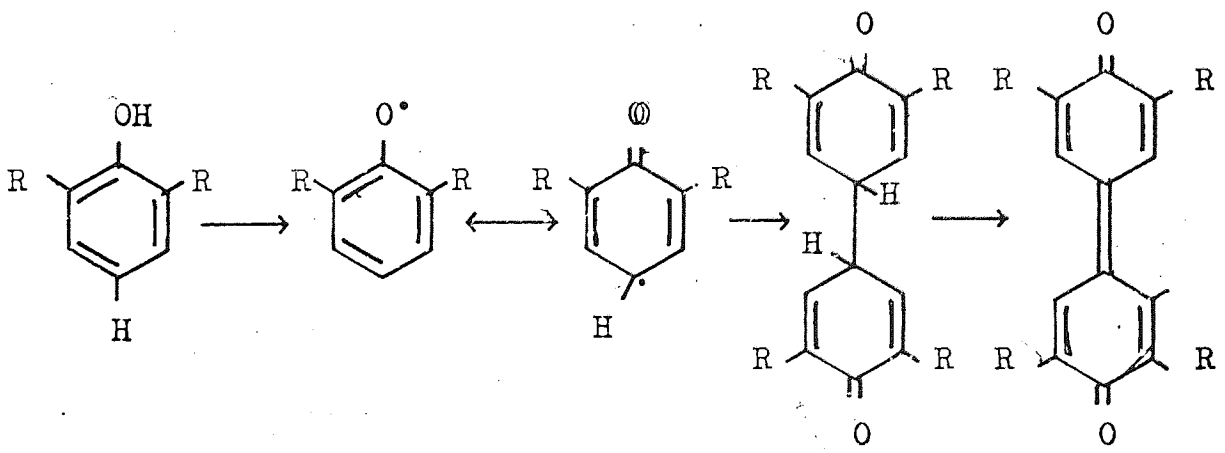
Analysis : Calculated for $C_{12}H_9ClO_2$, C : 65.45%, H : 4.1%,

found, C : 67.05%, H : 5.00%.

3,3',5,5'-TETRAALKYLDIPHENOQUINONES.

Coupling Reactions of Phenols.

2,6-Dialkylphenols may be coupled oxidatively to yield the corresponding 3,3'5,5'-tetraalkyldiphenoquinones. The mechanism is thought to proceed via a free radical intermediate as in VI in the general reaction scheme below;



V VI.a. VI.b VII VIII

A variety of oxidising agents have been used for these coupling reactions and their advantages or disadvantages are discussed in the literature (42).

Commonly used oxidising agents are potassium ferricyanide, (50), chromiumtrioxide and other inorganic oxidising agents (51,52), benzoyl peroxide (53), or a silver carbonate and Celite reagent that has been recently found to have application in phenolic coupling reactions of this nature (54). The difference between these reagents in terms of efficiency and yields of coupled products have been found to be minimal. The method used in this work, therefore was chosen for its simplicity, and that in all cases, the yields were in excess of 90% of products of extremely high purity. The oxidant used was chromium(VI)oxide (chromium trioxide) according to the method of von Auwers and Markowitz (52).

1g of the 2,6-dialkylphenol to be coupled were dissolved in $50cm^3$ of glacial acetic acid. 1g of chromium(VI)oxide was taken up in the minimum quantity of hot water, then made up to $50cm^3$ with cold glacial acetic acid. The phenolic solution was magnetically stirred while the oxidising solution was run in from a burette, cautiously over a period of half an hour. On completing the addition, the reaction mixture was warmed to $60^{\circ}C$ for an hour, then cooled in an ice bath. Crystals of the desired product separated on cooling and these were filtered and recrystallised from either benzene or glacial acetic acid.

14. 3,3',5,5'-Tetramethyldiphenoquinone.

1g of 2,6-dimethylphenol (2,6-xylenol) was coupled using the method outlined above. 0.92g of fine red needles were

yielded after recrystallisation from acetic acid, m.p.214°-215°C(decomp.), lit.val.215°C(54) with decomposition.

Analysis : Calculated for $C_{16}H_{16}O_2$, C : 80.00%, H : 6.67%,
found, C : 79.40%, H : 6.95%.

15. 3,3',5,5'-Tetramethoxydiphenoquinone.

2,6-Dimethoxyphenol was coupled according to the general method to give fine steel-blue needles upon recrystallisation from benzene, m.p. 192°C, lit.val. 193°C (51).

Analysis : Calculated for $C_{16}H_{16}O_6$, C : 63.16%, H : 5.26%,
found, C : 62.55%, H : 5.76%.

16. 3,3',5,5'-Tetraisopropyldiphenoquinone.

The same method was utilised in this

The same method was utilised in this preparation, with 1g of 2,6-diisopropylphenol as starting material, and yielded bright crimson platelets when recrystallised from glacial acetic acid, m.p. 194°-195°C, lit.val. 196°-197°C (55).

Analysis : Calculated for $C_{24}H_{32}O_2$, C : 81.81%, H : 9.09%,
found, C : 82.40%, H : 8.95%.

17. 3,3',5,5'-Tetra-sec-butyldiphenoquinone.

This compound was prepared as above from 2,6-di-sec-butylphenol and was isolated as lustrous deep red platelets after recrystallisation from benzene, m.p. 180°-185°C (decomp.) lit.val.185°C (33) with decomposition.

Analysis : Calculated for $C_{28}H_{40}O_2$, C : 82.33%, H : 7.79%,
found, C : 82.70%, H : 8.10%.

18. 3,3',5,5'-Tetra-tert-butyldiphenoquinone.

The general method was again used in this preparation and the product was obtained as a red-brown crystalline material on recrystallisation from glacial acetic acid, m.p. 244°C, lit.val. 246°-247°C (56).

Analysis : Calculated for $C_{28}H_{40}O_2$, C : 82.33%, H : 7.79%,
found, C : 81.00%, H : 8.40%.

B. Electron Spin Resonance Spectroscopy.

Instrumentation and Techniques.

1. The Spectrometers.

The majority of the e.s.r.spectra shown here were recorded on a Japan Electron Optics Limited (JEOL) PE-1X type spectrometer operating in the X-band microwave region. On this machine, spectra may be recorded at one of two modulation frequencies, 100KHz for normal high sensitivity measurements, and 80MHz for measurements at reduced temperature.

Automatic frequency control is an incorporated feature of the machine, allowing the klystron frequency to be locked to the resonant frequency of the sample cavity.

The spectrometer sample cavity is a high ⟨Q⟩ cylindrical reflection cavity operating in the TE_{011} mode. Various facilities are incorporated into the cavity to enable a number of operations to be easily carried out. A port in the side of the cavity enables the insertion of a standard sample, in this case, a manganous salt. An inlet and outlet system allows a stream of nitrogen (for heating and cooling purposes) to be passed and a removable cover exposes a window for u.v.irradiation.

Detection, when recording, is by hot carrier diode, which enhances sensitivity at low modulation frequencies. A video display unit allows rapid scanning and troubleshooting during setting up and prior to recording the spectrum, in this system the method of detection is by phase sensitive detector.

The recording system incorporated into the spectrometer is a digital DYT recorder, with three operational modes : firstly, in the DY mode, the chart roll is fixed and the pen-bar scans the spectrum through the predetermined field sweep (ranges from $\pm$ 0.25G to $\pm$ 1000G); in the DYT mode, the pen-bar scans the spectrum as before, but the chart roll is also moved, in the opposite direction, enabling the spectrum to be magnified 1.5, 2 or 3 times the original size; finally, operation in the YT mode fixes the pen-bar while moving the chart roll, thus enabling the measurement of reaction rates and kinetic studies by setting the pen-bar at some point in the spectrum and following the rate of increase or decrease in intensity of a particular linein the spectrum..

All other e.s.r.measurements were made on a Hilger and Watts 'Microspin' X-Band Spectrometer, the details of specification and operation of which may be found elsewhere (57).

2. Sample Preparation.

The sample tubes used in the e.s.r.measurements were either of whole lengths of 'Spectrosil' quartz tubing (o.d.4.5mm)

or were the standard JEOL sample tubes, consisting of a 10cm length of thin-walled quartz tubing (o.d.5.0mm.) topped by a 10cm length of glass tubing of similar diameter.

If required, deoxygenation of the e.s.r. samples was aided by the topping of the sample tubes with B-10 stoppers, which facilitated their connection to a vacuum line. Deoxygenation was effected by a repetitive freeze-thaw technique, the maximum number of freeze-thaw operations being three. Work by Dudley(58) has shown that, when using this technique for the deoxygenation of solvents and solutions, three freeze-thaw operations remove the highest proportion of oxygen, and further operations have little effect and no more oxygen is extracted.

Preparation of Diphenosemiquinone Cation Radicals.

Cation free radicals were prepared by either of two methods : Firstly , by the reduction of the parent quinone by a trace of sodium dithionite in concentrated sulphuric acid ; or secondly, by the oxidation of the corresponding hydroquinone with a trace of hydrogen peroxide in the same solvent.

A known mass of the quinone or diol to give a concentration in the range 0.001 - 0.005M was added to $2cm^3$ of 98% conc. sulphuric acid. The resulting solution, deoxygenated if necessary, could be examined in the spectrometer.

Cation radicals prepared by the oxidation of biphenyl-,4,4'-diols and those prepared from 4,4'-dialkoxy- and diaryloxy-

biphenyls were prepared in concentrated sulphuric acid to which a trace of hydrogen peroxide or potassium persulphate had been added prior to the addition of substrate. If the oxidant is added after the addition of substrate, then complex sulphonation reactions occur (33).

When the radicals are produced by the reduction of the diphenoquinone, no reducing agent is necessary, unless the radical concentration is small whereby an increase may be affected by the addition of a small amount of sodium dithionite.

Preparation of Diphenosemiquinone Anion Radicals.

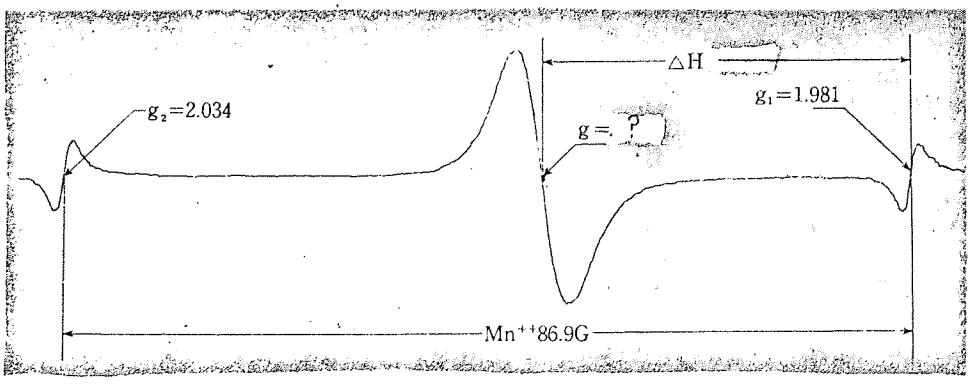
These radicals were produced in a solvent mixture of 2M potassium hydroxide and pyridine mixed 1 : 1 by volume. The solvent composition was varied when studying some selected tetraalkyldiphenosemiquinone anions (chapter 5.). The air oxidation of the biphenyl-4,4'-diol or the biphenyl-2,4,4'-triol yielded the required semiquinone anions in some examples, while in the same solvent mixture the radicals may be produced directly from the corresponding quinone by a mechanism involving the reduction of the quinone, which yields a mixture of semiquinone anion and diamagnetic dimer, the concentration of the semiquinone anion being enhanced by the addition of the electron donating organic solvent (59).

The e.s.r.samples were prepared by dissolving the requisite amount of parent compound, to give a concentration of 0.001 - 0.005M, in $1cm^3$ of solvent.

3. Measurement of g-Values.

The standard sample in the JEOL PE-1X system is a sample of a manganous (Mn^{++}) salt, enclosed in a holder which may be inserted into the sample cavity through a port provided for this purpose.

Mn^{++} has a nuclear spin of $\frac{5}{2}$ and the e.s.r.spectrum has $2N + 1 = 6$ lines. These lines are evenly spaced, 86.9G apart and it is found that most organic free radical resonances occur between the third and fourth lines of the Mn^{++} spectrum. The g-value of an unknown sample is readily calculated using the field deviation, ΔH, between the centre of the unknown resonance and the fourth line of the Mn^{++} spectrum. ΔH is precisely determined by comparing the position of the unknown spectrum with the peak interval of 86.9G between the third and fourth lines of the standard.



From the diagram

$$g = \frac{g_1 H_1}{H + \Delta H}$$

where g is the g-value of the unknown sample,

g_1 is the g-value of the standard peak(1.981 @ 9,300MHz)

H is the value of the field at the unknown peak,

Δ H is the field deviation of the unknown and standard peaks.

CHAPTER THREE.

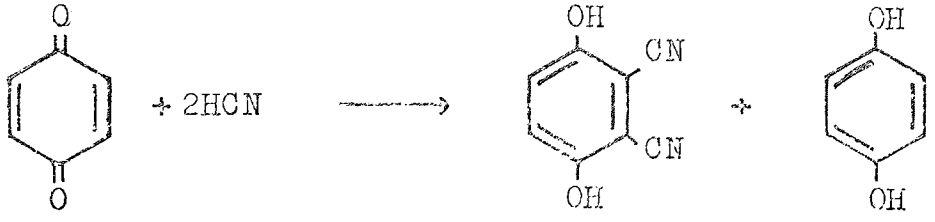
ASPECTS OF THE ADDITION AND SUBSTITUTION CHEMISTRY OF 4,4'-DIPHENOQUINONES.

Part I : Cyanide Addition and Substitution.

The methods by which cyano- groups may be introduced into organic molecules are many and varied, much is understood of the reactions and their mechanisms, and they have been well summarised (59). Little however, has been understood about the addition of cyano- groups to quinones since the early experiments of Thiele and Meisenheimer (60) and the first reasonable attempts to describe the mechanistics of the addition of hydrogen cyanide to 1,4-benzoquinone were not made until the work of Wallenfels et Al., in 1965 (12).

A. The Addition of Hydrogen Cyanide to Quinones.

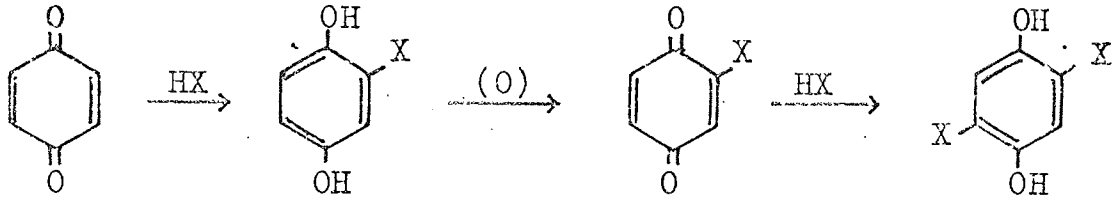
The experiments of Thiele and Meisenheimer (60) found that, unlike the addition of the apparently similar hydrogen halides to 1,4-benzoquinone, addition of hydrogen cyanide yielded solely the 2,3- diaddition product,



no monoaddition product could be isolated, and it was

subsequently ascertained that the reaction only takes place in the temperature range 20°C - 30°C (61).

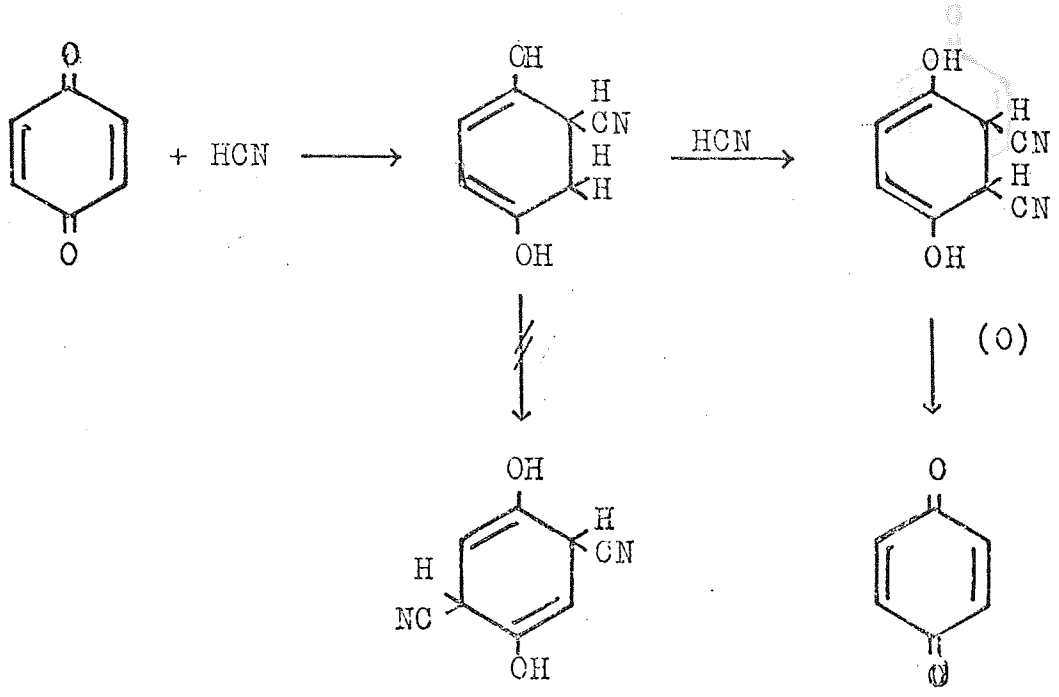
Reactions between 1,4-benzoquinones and reagents of the type HX are thought to proceed by a 1,4-addition process to the O=C-C=C- system, the intermediate first enolising and then being reoxidised to the quinone by a further 1,4-benzoquinone molecule, then the mono-X-quinone adds another HX molecule to yield the 2,5-di-X-hydroquinone.



A similar mechanism has been proposed for the addition of hydrogen cyanide to 1,4-benzoquinone with the modification that the cyano- group already present directs the second group to the ortho- position (61). However, this interpretation is unlikely because the reaction would involve the formation of 2-cyano-1,4-benzoquinone, which has a higher oxidation potential than the unsubstituted compound. Also, 2-cyano-1,4-benzoquinone has been synthesised and found to be extremely water sensitive and does not survive in aqueous reaction media (62).

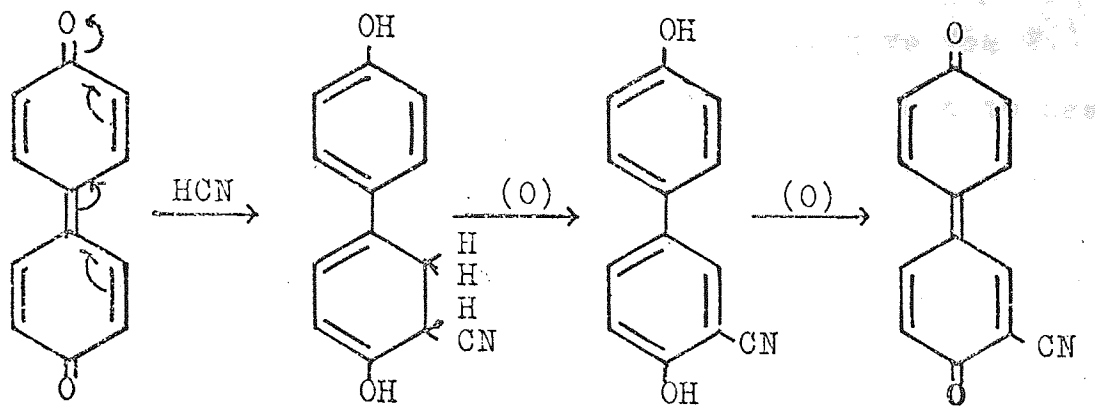
A more feasible mechanism for this reaction has now been recognised (12) involving the second addition of hydrogen cyanide to be 1,6- , giving the 2,3-dicyano-2,3-dihydro-

hydroquinone, which is then oxidised to the 2,3-dicyano-benzoquinone (fig.3.1.).



3.1.

If a mechanism of this type could now be applied to the 4,4'-diphenoquinone system, it may result in the formation of the previously unknown cyano-substituted diphenoquinones. If it is assumed that the addition of cyano- groups to the 2,6,2',and 6' positions is not possible on steric grounds, the most likely place of addition would be the 3 and 5 positions in either ring. This may be thus interpreted as being a 1,8-addition process as in figure 3.2. In the reaction, III would not be reoxidised by excess quinone, so for further addition to occur, III would have to be isolated then oxidised to the quinone IV by means of an inorganic oxidant in order to attempt further additions.



I II III IV

3.2.

As no previous attempts to add hydrogen cyanide to diphenoquinone have been reported, the practical methods of Wallenfels (12) for the addition to 1,4-benzoquinone were followed where possible, making modifications if necessary.

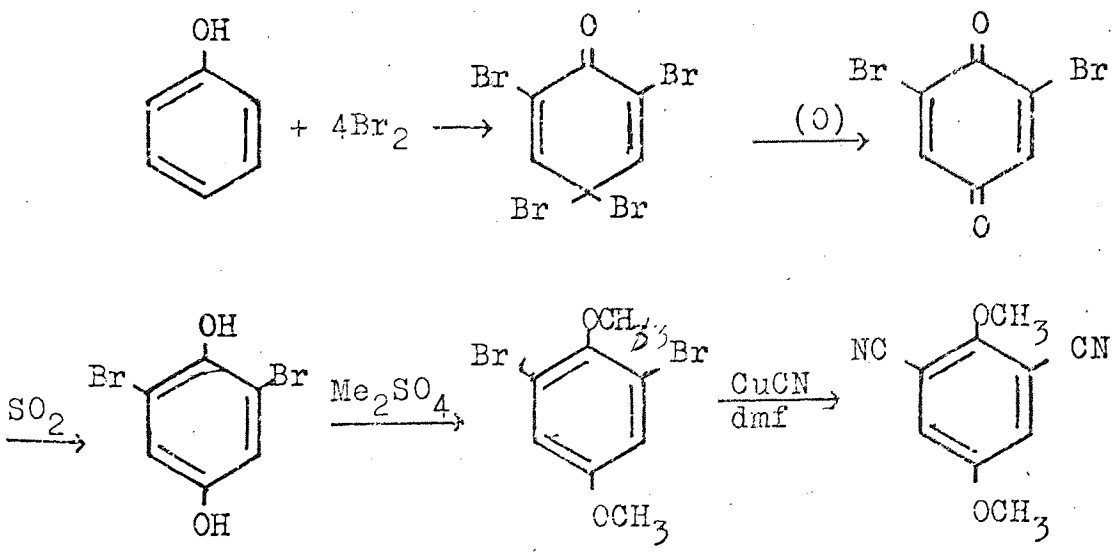
B. Substitution in Quinones by Hydrogen Cyanide and Cyanide Ion.

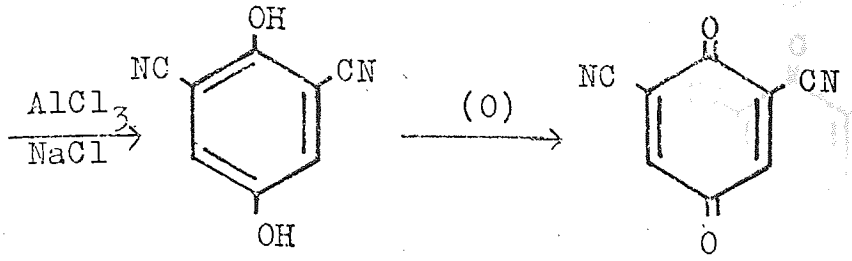
The kinetics and mechanism of the substitution of halogenated 1,4-benzoquinones by cyanide ion were first summarised in 1961 (62), and it was found for example, that treatment of chloranil with potassium cyanide in ethanol yielded dichlorodicyanobenzoquinones, which could be further substituted to yield tetracyanobenzoquinone.

In order to prepare 2,5- and 2,6-dicyano-1,4-benzoquinones, Wallenfels et Al.(12)formulated two synthetic routes which involved the reduction of 2,5-diamidohydroquinone to give

involved the reduction of the 2,5-diamidohydroquinone to give the 2,5-dicyanobenzoquinone and the substitution of a 2,6-dihalohydroquinone by cyanide ion to give the 2,6-dicyanobenzoquinone. These pathways were examined to assess their possible application to the analogous diphenoquinone systems.

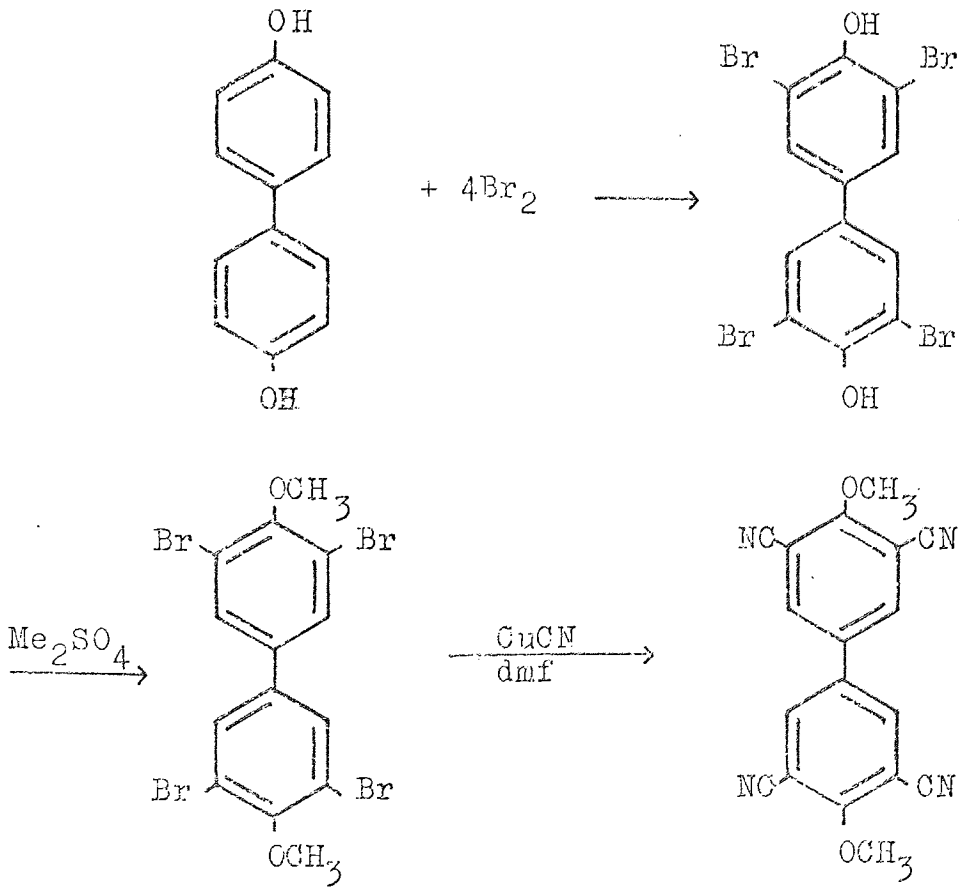
The reaction scheme most readily applicable for the synthesis of cyano-substituted diphenoquinones was found to be that for the preparation of 2,6-dicyanobenzoquinone. In the original synthesis, phenol is first brominated and then oxidised to 2,6-dibromobenzoquinone, which is then reduced to the corresponding hydroquinone. In order to prevent the hydroxyl groups from being replaced by cyano- groups they are methylated using dimethyl sulphate and the resulting dibromodimethylether is mixed with cuprous cyanide in dimethyl formamide to effect the substitution of the bromine atoms by cyanide ion. The dicyanodimethylether is then demethylated toyield 2,6-dicyanohydroquinone. The reaction is shown in figure 3.3.

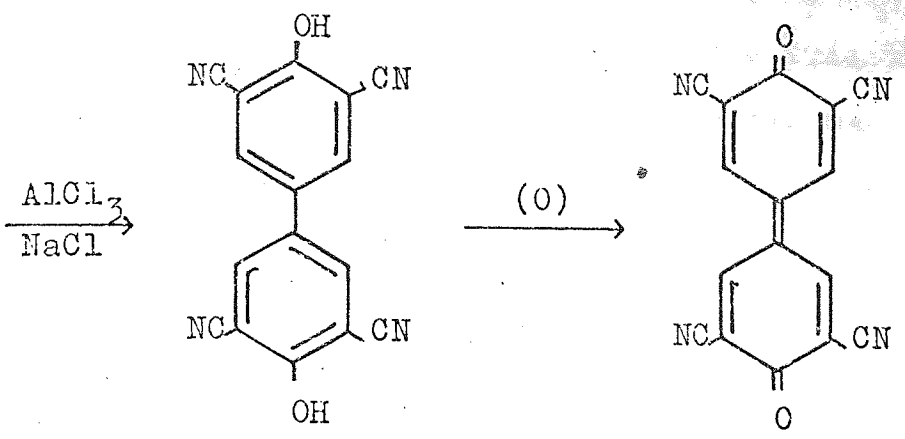




3.3.

This reaction scheme is readily modified to suit the diphenoquinone system due to the ease of formation of 2,2',6,6'-tetrabromobiphenyl-4,4'-diol, which is the sole product of the addition of bromine to a solution of biphenyl-4,4'-diol in hot glacial acetic acid (43,63). The tetrabromo-diol is readily methylated in cold alkaline solution using dimethyl sulphate, and the reaction is continued as in figure 3.4.

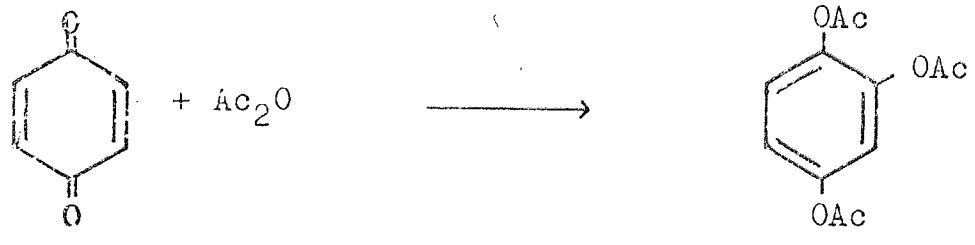




3.4.

C. The Thiele Acetylation of Quinones.

When 1,4-quinones are treated with acetic anhydride in the presence of a trace of concentrated mineral acid, a reaction proceeds with a combination of addition and esterification.



The reaction was first studued by Thiele in 1900 (64), and has since been widely used for the synthesis of new quinones, for proof of structure of quinones, and in the isolation and purification of natural products (19).

A series of papers on the kinetics of the Thiele acetylation of 1,4-benzoquinones has appeared (65), showing the reaction

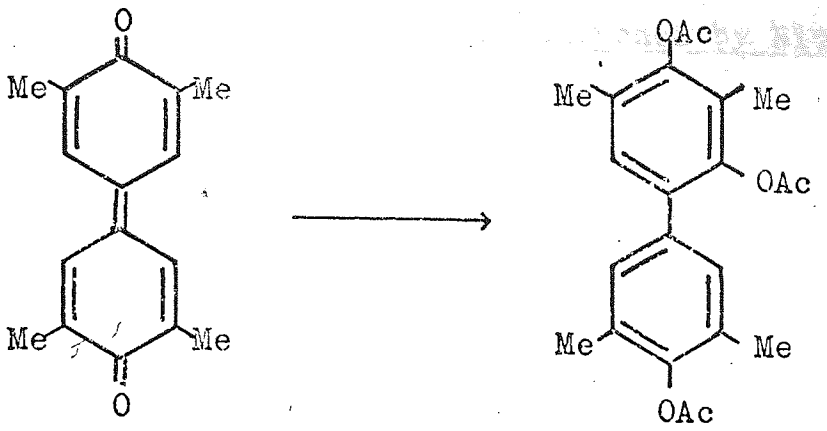
mechanism to be complex. In nearly pure acetic anhydride, the above reaction yields only 1,2,4-triacetoxybenzene, but in acetic anhydride with more than two per cent of acetic acid present, further significant products, 1,4-diacetoxybenzene and 1,2,4,5-tetraacetoxybenzene, are formed. In the light of all recent evidence, the additional products, and the thermodynamics and behaviour of the solvent system, it is now concluded that the major species involved in the acetylation is the acetylinium ion,

$$Me-\overset{\overset{O}{\|}}{C}_{+}$$

The practical details of the reaction and the direct formation of the corresponding hydroxy- substituted compounds without the isolation of the acetylated products, are discussed in chapter two.

The Thiele acetylation as applied to diphenoquinone has yet to be characterised, although one reaction on a substituted diphenoquinone has been reported, in a paper titled 'The Reactivity and Product Orientation in the Thiele Acetylation of Quinones' by Erdtmann (67). The product obtained from the acetylation of 3,3',5,5'-tetramethyldiphenoquinone and subsequent hydrolysis by sodium hydroxide was shown to be the tetramethyltriol, III in the reaction in figure 3.5

Using similar experimental methods, the reaction is applied to other alkylated diphenoquinones to attempt to prepare compounds related to III, and also attempts were made to



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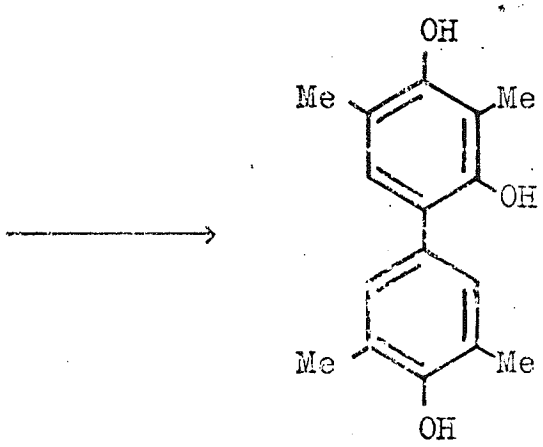


III.

characterise the reaction on unsubstituted diphenoquinon;

D. Addition and Substitution of Quinones by Nitrogen Containing Groups.

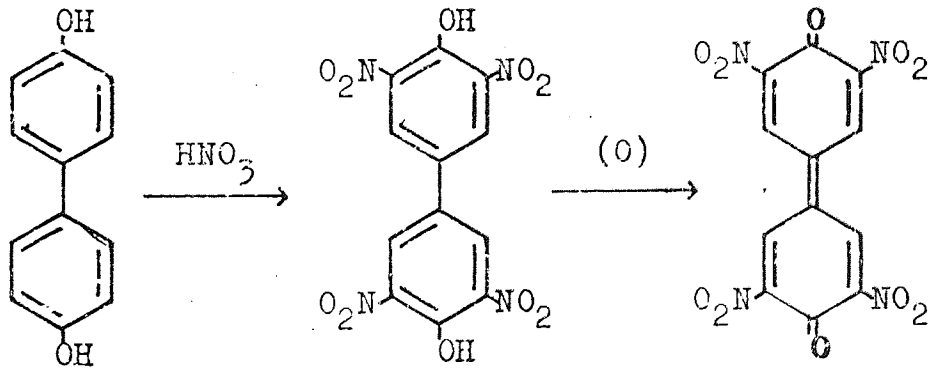
The addition of nitrogen-containing substrates and the reactions of substituted quinones with such reagents has been well reviewed (19). Several nitrogen containing compounds (amines, azides, heterocyclic compounds etc.) add directly to unsubstituted 1,4-benzoquinone to yield products in which the nitrogen atom is bonded to the benzene ring. The mechanism of these additions have been found, in general, to be Michael type addition processes giving the hydroquinones which are then oxidised with the usual inorganic oxidants to the corresponding quinones. No similar reactions have been reported involving additions to diphenoquinones and attempts were made here to apply the Michael addition to diphenoquinones.

Several reactions involving additions and substitutions of amino- type compounds to 1,4-benzoquinones were examined and applied to the corresponding diphenoquinones. These reactions are summarised in table 3.6.

Substituent	1,4-benzoquinone upon which the reaction was previously performed	Ref
Methylamine	unsubstituted and methyl and methoxy-	19.
Dimethylamine	unsubstituted	19.
Ethylenediamine	- „ -	68.
Piperidine	unsubstituted and halogenated	69.
Ethylene imine (aziridine)	- „ -	18.

3.6. Substitution of 1,4-benzoquinones by aliphatic amines

The only diphenoquinone with substituents with nitrogen bonded to the quinone rings previously reported is prepared by the action of concentrated nitric acid on biphenyl-4,4'-diol (63), followed by oxidation.



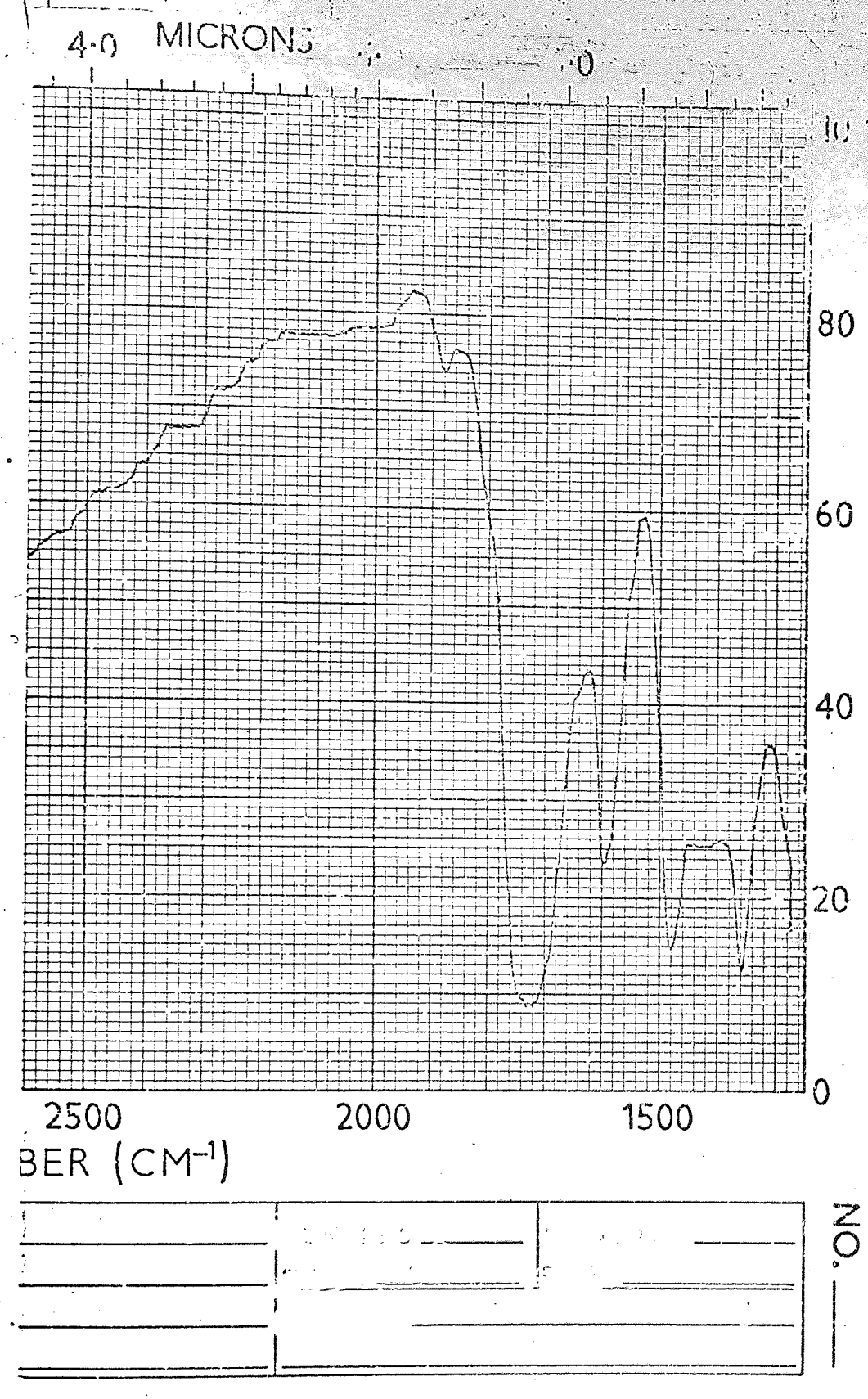
Attempts were made to reduce the nitro- groups to amino-groups but these proved unsuccesful.

Part II : Results

A. The Addition of Hydrogen Cyanide to Diphenoquinone.

The reaction was carried out as described earlier, by the method of Wallenfels (12) involving the action of cyanide ion (from potassium cyanide) on unsubstituted diphenoquinone.

No cyano- substituted diphenoquinones were isolated after this reaction. CHN analysis results were not consistent with those expected and no C≡N stretching peak was observed in the infrared spectra. Spectrum 3.1 shows the infrared region from 2,200cm^{-1} to 3,000cm^{-1} and no sharp peak for the C N stretch is observed where it might be expected, between 2,200cm^{-1} and 2,250cm^{-1} (the product which produced this spectrum was isolated from the reaction carried out at 35°C, but all the products gave a similar result). The temperature at which the reaction was carried out was varied to 100°C, but little difference in analysis resluts was observed. In the addition of cyanide ion to 1,4-benzoquinone the reaction only proceeds in the temperature range 20°-30°C but here this was extended. Products obtained from reactions at 25°, 35° and 65° were extracted and analysed, but CHN analysis, infrared spectra and mass spectrometry measurements were again inconclusive. The mass spectra of these samples showed a parent ion peak at m/e 184, identical to that of diphenoquinone, and no peaks at all between this value and m/e 314, the expected value of the parent ion peak of tetracyanodiphenoquinone (which might be formed if more than



3.1. The infrared spectrum of the product of the reaction between diphenoquinone and potassium cyanide. No C≡N stretching band is observed.

the cyano- group could be introduced into the molecule, although this is unlikely.

B. The Substitution of Diphenoquinones by Cyanide Ion.

The reaction set out in figure 3.4. was used in this synthesis, the starting material for the cyanide substitution step being 3,3',5,5'-tetrabromo-4,4'-dimethoxybiphenyl. The organic products were separated and recrystallised to constant melting point, then analysed by infrared spectroscopy and mass spectrometry. The parent ion peak in the mass spectrum was at m/e 586, which corresponds to that of the starting material. Again the temperature of the reaction was varied and products isolated at other temperatures were found to give similar results to those above. The reaction was carried out in dimethyl formamide and the temperature varied between 120° and 140°C (b.p. of D.M.F.is 144°C). The use of higher boiling point solvents was precluded because the melting point of the starting material is 150°-155°C with decomposition.

C. The Thiele Acetylation of Diphenoquinones.

The practical details of these reactions are outlined in chapter two, but the method used was similar to that described in Vogel's 'Practical Organic Chemistry'(46), using either concentrated sulphuric acid or perchloric acid as catalyst.

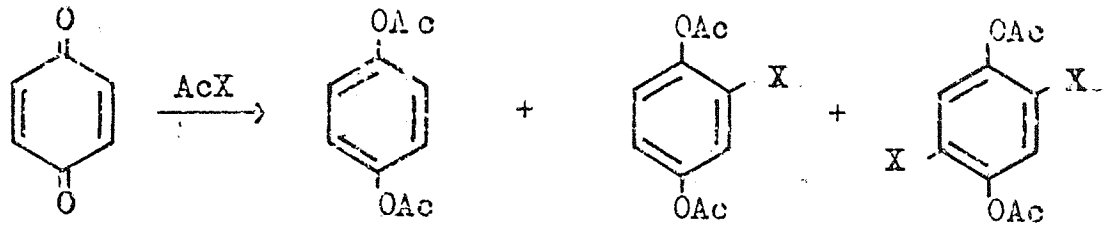
When the reaction is carried out on diphenoquinone, three

products may be isolated by extracting the reaction mixture with methanol, then acetone, leaving a solid residue. The acetone extract yielded unreacted diphenoquinone while after recrystallisation, the methanol extract gave a pale brown solid. The analysis results (CHN) gave totally incomprehensible results and the infrared and n.m.r.results were also confusing appearing to be indicative of the presence of several acetyl groups. However all attempts to purify this product failed due to its instability. After one day, the solid begins to darken in colour and continues to do so, whilst smelling strongly of acetic anhydride, until a highly coloured purple solid remained.

A possible explanation for these observations could be that, the original product being a mixture of several acetylated biphenyls, which are unstable and are oxidised, with the loss of the acetyl groups at positions 4 and 4' to give the corresponding diphenoquinones. This might explain both the evolution of acetic anhydride and the formation of the strongly coloured residue. The residue might then be a mixture of acetylated diphenoquinones, practically difficult to separate due to the number of products possible and their isomers, which might be expected to have similar properties.

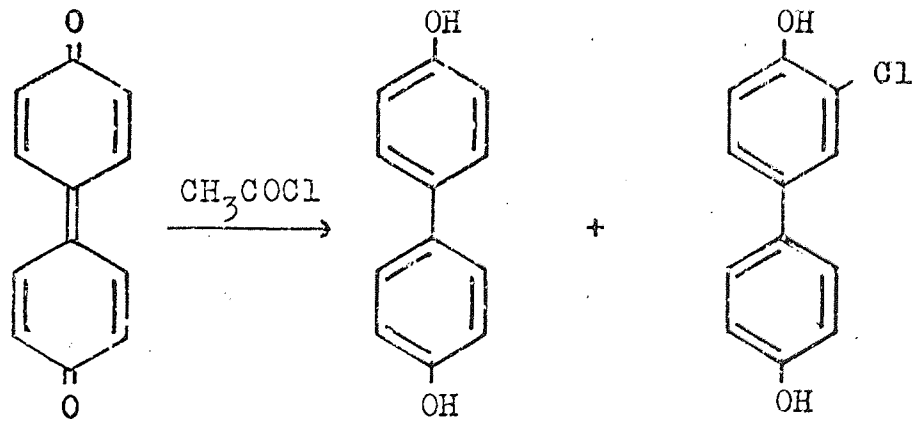
In the acetylation of 1,4-benzoquinone, the products are different when the mineral acid used as catalyst was changed to perchloric acid from sulphuric acid. When this change was made in the reaction for diphenoquinone, no change in the results reported above was noted.

Conclusive results have been obtained when diphenoquinone is acetylated by the action of acetyl chloride. The reaction between 1,4-benzoquinone and acyl halides was known before the experiments of Thiele by two groups of workers(70,71), who found that when 1,4-benzoquinone was treated with acetyl chloride or bromide, in the presence of a mineral acid, mono- and di-halogenated diacetylbenzenes were formed (fig.3.7.).



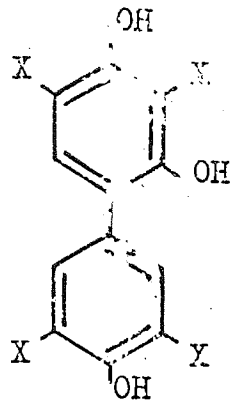
3.7.

When this reaction is carried out on diphenoquinone, and is followed by deacetylation, the sole products formed are biphenol-4,4'-diol and 3-chlorobiphenyl-4,4'-diol



The acetylation of alkylated diphenoquinones was mentioned earlier in the chapter. Successful reactions were carried

out according to the method of Erdtmann (67) in order to prepare compounds of type V, where X represents Me (VII) OMe(VI)and t-Bu (VII).



V

D. Addition of Nitrogen Containing Substituents.

These reactions, involving the addition of methylamine, dimethylamine, ethylenediamine, piperidine and ethylene imine, were largely unsuccessful. The additions of methylamine and ethylenediamine however, did succeed in producing thick red oils, but these proved impossible to extract and purify without decomposition. In all the reactions, the solvents and quantities of reactants were varied and the t temperature was elevated where possible, but these had no effect on the outcome of the reactions.

A reaction involving the substitution of the methyl groups in 3,3',5,5'-tetramethyldiphenoquinone by the azide ion (N_3^-), using sodium azide, was also unsuccessful. The reaction proceeds quite readily on the corresponding 1,4-benzoquinone and is well reported (19).

Part VIII; Discussion.

Despite one or two successes, the addition and substitution reactions examined in this work have proved to be largely unsuccessful. However the failure of these reactions can lead us to make some general observations on the reactivity of diphenoquinones.

A major factor in the hindrance of these reactions must be the high value for the oxidation potential of diphenoquinone itself. Vigourous conditions are needed to bring about substitution in the diphenoquinone rings, added to the fact that substitution in the 2 and 6 positions in either ring must be restricted on steric grounds.

The main object of this work has been to attempt to prepare diphenoquinones with extremely high oxidation potentials, in order that they might achieve similar importance in organic synthesis as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has done. However such high potential quinones are necessarily unstable and difficult to prepare because of their high oxidation potentials. From the evidence for tetracyanobenzoquinone, which, although isolable, is extremely unstable and water sensitive due to its high oxidation potential, we might expect that had these syntheses been successful, similarly difficult to handle and highly unstable compounds may have resulted.

It may be said that the only diphenoquinone yet to have

found any significant use in areas of organic and inorganic synthesis is 3,3',5,5'-tetrachlorodiphenoquinone, which has the highest oxidation potential of all known stable quinones (compare tables I and II in chapter one)

Although the acetylation of diphenoquinone was successful when acetyl chloride was used as the acetylating agent, the Thiele method was largely unsuccessful, and the characterisation of products produced in this latter case proved to be difficult. Controlled conditions of acetylation could only be produced where the position of the incoming acetylinium ion was directed to a high degree, i.e. in the acetylation of tetraalkyldiphenoquinones. This again may be partially due to the comparitively low oxidation potentials of the diphenoquinones under acetylation. It has been found that for 1,4-benzoquinones, substitution by highly electron withdrawing groups such as the acetyl group generally leads to controlled selective addition or substitution. However, the case appears to be more complex for diphenoquinones. The oxidation potentials of the tetraalkyldiphenoquinones are tabulated in chapter one, and the values are clearly of the order of some of the benzoquinones that are readily acetylated.

The failure of the nitrogen containing nucleophiles to add to diphenoquinones is a little surprising. Extensive results for 1,4-benzoquinones have shown that a series to show the ease of diplacement of quinonoid substituents by amines may be compiled (19),

F >  > OR > OAr > SR > OAc > Br, Cl

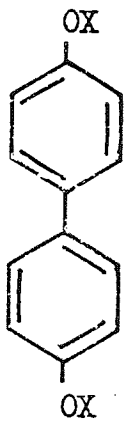
and in the light of this it may be expected that some degree of substitution might be expected for similarly substituted diphenoquinones, but the products obtained from the addition of methylamine and ethylenediamine may give a clue to the difficulty of formation of these compounds.

The results of the acetylation of diphenoquinone by acetyl chloride give the only insight to the addition and substitution chemistry of diphenoquinones. It is thought that in this case the 1,8-addition process described earlier in the chapter may be operative.

CHAPTER FOUR

STUDIES INVOLVING SLOW AND RESTRICTED INTRAMOLECULAR ROTATION EFFECTS IN DIPHENOSEMIQUINONE AND RELATED RADICAL IONS.

This study involves the examination of diphenosemiquinone anions and cations. The cation radicals exhibit restricted rotation about the C_4- O (and $C_{4'}$- O) bond and also the O-X bond in compounds of type I, while the anion radicals show the same effect about the C_1- $C_{1'}$ ring linkage.



Firstly, the theoretical considerations necessary for a primary understanding of the results are explained, experimental observations are then noted and then the conclusions are discussed in two parts at the rear end of the chapter.

Part I : The Alternating Linewidth Effect.

Introduction.

In the years immediately after the inception of electron

spin resonance spectroscopy, much progress was made in the interpretation and understanding of spectra, and basic information about the hyperfine splitting and the nature and value of g for many different types of free-radical was obtained. It became apparent however, around 1960 that, with the improvement in the standard of instrumentation and techniques, some spectra may exhibit peculiar variations in linewidth from one component to the next. Since the amplitude of first derivative lines is proportional to the inverse square of the linewidth, small changes in linewidth may be readily observed. Although such linewidth changes may have hampered early e.s.r.experimenters, it soon became clear that with a deeper analysis, useful information might be obtained from the study of linewidths. This information includes data on topics such as ion-pair interactions (solvent effects included), inter and intramolecular processes and the π-electron distibution in radicals (27).

Linewidth variation may be apparent in a number of forms : lines may be broader on one side of the spectrum than the other; lines may broaden from the centre of the spectrum outwards; or as some external variable (e.g. temperature) is changed, all the lines may broaden. The most striking linewidth effect in e.s.r.spectroscopy arises from fluctuating hyperfine splittings due to an inter- or intramolecular process, this effect is termed the 'alternating linewidth effect'.

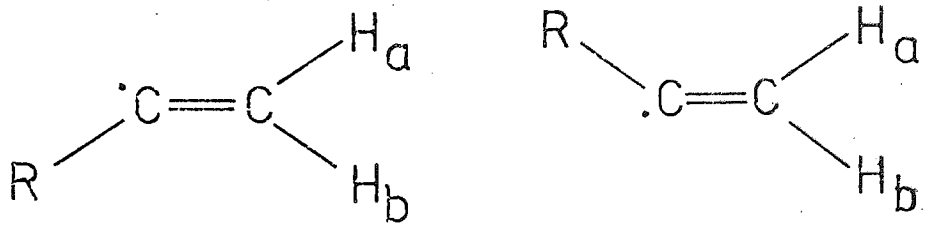
Two groups of workers were independently responsible for the discovery of the alternating linewidth effect. Bolton

and Carrington (26) found that the duroquinol cation showed linewidth alternation, while Freed, Bernal and Fraenkel discovered that the anion of the 1,4-dinitrodurene radical exhibited the effect (72).

A Simple Model.

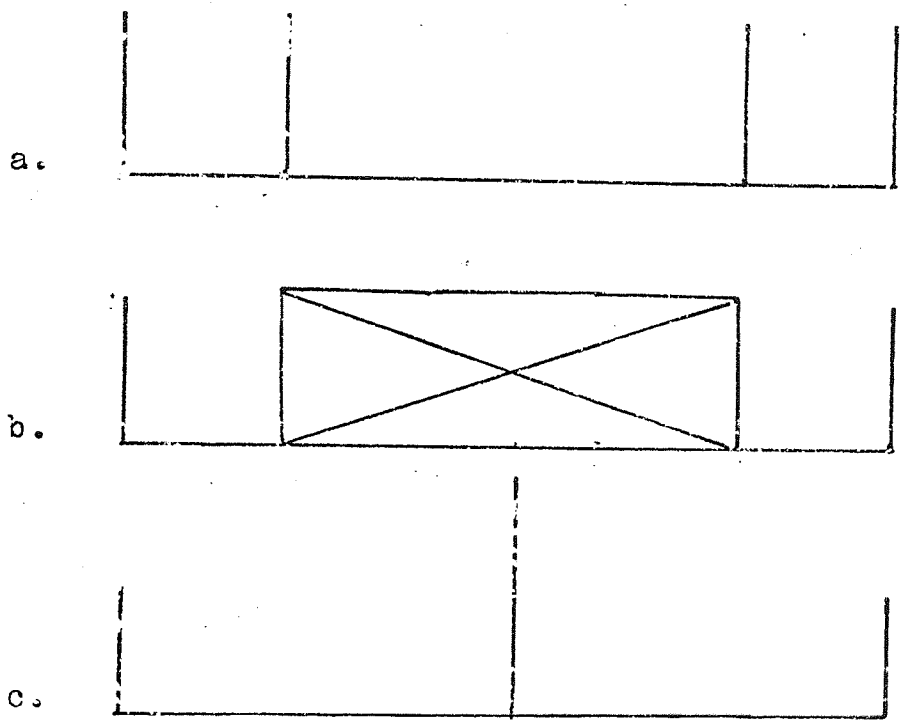
In a radical that has two nuclei with $I=\frac{1}{2}$, by Freed and Fraenkel (73) they are said to be 'completely equivalent' if their hyperfine splittings are the same at any instant. If the splittings are only the same however, when averaged over a period of time, they are said to be merely 'equivalent'. This latter condition may lead to an alternating linewidth effect, the basic requirement being that the two hyperfine splittings are anticorrelated (i.e. as one splitting increases the other decreases) so that their sum remains the same.

In the hypothetical vinyl radical as in figure 4.a. where the group R gives no splitting, the interconversion of I and II interchanges the splittings of the two protons H_a and H_b, and the rate of interconversion determines the shape of the spectrum.



4.a.

At a slow rate of interconversion between I and II, the two splittings of H_a and H_b are non-equivalent and are readily apparent in the e.s.r.spectrum. At a fast rate of conversion an average spectrum is obtained, the two protons seeming to be equivalent (see figure 4.b.)



4.b. Spectra for the hypothetical vinyl radical at a),slow, b), intermediate and c), fast rates of interconversion.

At intermediate rates of conversion (b, above),the centre line will appear broad while the outer lines remain sharp (if no nuclear spin transitions take place during the conversion of I to II). This is because the radicals contributing to the outside lines do not shift in resonance frequency on conversion since their line positions are proportional to $(a_1 + a_2)$, the sum of the two hyperfine splittings. Those radicals contributing to the centre line in b), do shift in resonance frequency sinc their line positions are proportional to $(a_1 - a_2)$. This broadening can be shown to

be proportional to $\tau((\delta H)^2)$ where τ^{-1} is the average first order rate constant for the interconversion process and $((\delta H)^2)$ is the mean square variation in line position as a result of the hyperfine splitting fluctuations i.e. $\delta H = \frac{1}{2}|(a_1 - a_2)|$. Russell and co-workers (74) have found that the anion of 3,3-dimethylcyclohexanedione gives results similar to this hypothetical case. At -80°C the fixed rotation case is observed, while at +90°C the time averaged spectrum can be observed and at intermediate temperatures the outer lines remain while the centre line is broadened.

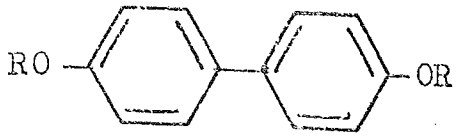
From this introduction it can be seen that, in any study of intramolecular rotations, and the observation of such effects by e.s.r., a knowledge of the alternating linewidth effect is fundamental in order to enable full interpretation of the spectra and to make theoretical deductions from them.

Part II : Present Work.

Compounds derived from diphenoquinones and biphenyl-4,4'-diols were prepared that may be expected to yield dipheno-semiquinone type radicals that exhibit the alternating linewidth effect.

A. Cation Radicals.

In their review article on the alternating linewidth effect, Bolton and Sullivan (27) predicted that compounds derived from biphenyl-4,4'-diol thus,

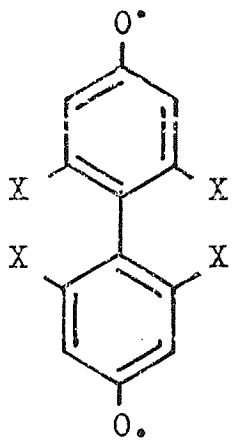


where R is an alkyl or aryl group, might give free radical species that may show intramolecular slow rotation about the 1 - 1' bond. If this prediction were correct and such conditions did exist, then the e.s.r. spectra of these radicals could be expected to exhibit some degree of linewidth alternation. Subsequent practical examination of these species could then be used to validate the numerical and theoretical analyses of such effects of Petersen (75) and Fraenkel (76).

It has been shown that (33,34) when biphenyl-4,4'-diol is oxidised in 98% concentrated sulphuric acid, the resulting e.s.r.spectrum shows no hyperfine splitting from the hydroxyl protons and no linewidth alternation arising from restricted rotation about the 1 - 1' bond. The spectrum, now recognised as being that of the diphenosemiquinone cation radical, arises from the interaction of two groups of four equivalent protons and consists of seventeen equally spaced lines ($a^{H}_{2,6}$ = 2.05G, $a^{H}_{3,5}$ = 0.71G). It was decided therefore, to prepare compounds where R above is methyl, ethyl, phenyl and p-nitrophenyl, and examine them in the same reaction medium to observe any slow rotation phenomena about the 1 - 1' bond and, if no such effects were present it may be possible, with the increasing bulkiness of R, to observe restricted rotation about the C_4 - O bonds or the O - R bonds.

B. Anion Radicals.

Although before the discovery of the alternating linewidth effect and intramolecular slow rotation phenomena, and their observation by e.s.r.spectroscopy, Bourdon and Calvin (39) attempted to restrict rotation about the 1 - 1' bond in substituted diphenoquinones by steric methods. By the substitution of the 2,2',6 and 6' positions with as many bulky alkyl groups as possible, it was hoped that non-planar, rigid diphenoquinones would be formed which, when reduced in the suitable reaction media would yield anion diradicals of type III.



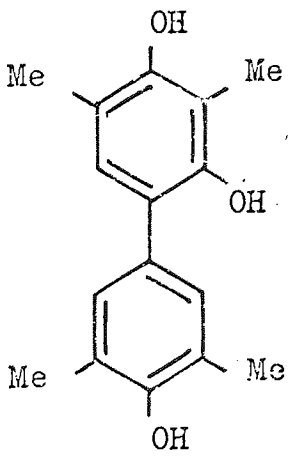
III

As the 1 - 1' bond would be fixed, no interaction of the free electrons could occur across the ring linkage, so it is reasonable to assume that both carbonyl groups would be reduced independently to give the required diradical. Owing to the rather primitive instrumentation available at that time the results of the work proved to be inconclusive, but in one example that of 2,2'-di-tert-butyl-5,5'-dimethyldiphenoquinone, it was deduced from magnetic susceptibility

measurements that the quinone may have been in equilibrium with a small amount of diradical.

Investigating the work of Bourdon and Calvin (39) it was concluded that diphenoquinones substituted in the 2,2',6 and 6' positions are practically difficult to prepare. Other alkyl substituted diphenoquinones (substituted in the 3 and 5 positions)are in general prepared by phenolic coupling reactions. Starting with 3,5-dimethylphenol or 3,5-di-tert-butylphenol, no coupled products can be obtained using conventional inorganic oxidants. Attempts to prepare the diphenoquinones mentioned in the work of Bourdon and Calvin also failed.

While undertaking an extensive study of syntheses and the mechanistics of the Thiele Acetylation of carbonyl compounds, H.G.H.Erdtmann performed the acetylation on 3,3',5,5'-tetra-methyldiphenoquinone, and after the isolation of the resulting triacetoxy compound followed by alkaline hydrolysis, IV, the tetra methyltrihydroxybiphenyl was isolated.

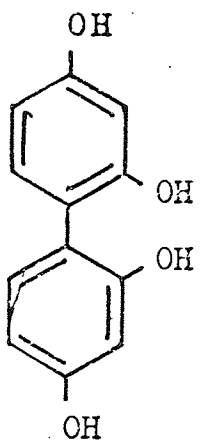


IV

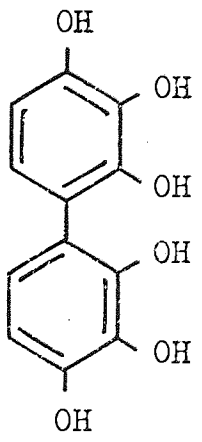
Theoretical discussion of the Thiele Acetylation is in chapter three while practical details are described in chapter two.

IV was prepared in order to observe its behaviour on air oxidation in a solvent mixture of 2M potassium hydroxide and pyridine (1 : 1 by volume), and to detect and characterise the e.s.r.spectra of any radicals so produced. A series of similar compounds were produced for the same purpose, these being the tetra methoxy- and tetra-tert-butyl analogues of IV.

Also, a commercial sample of compound VII was obtained, and attempts to prepare VIII by the oxidative couplig of 1,2,3-trihydroxybenzene (pyrogallol) failed. These two compounds were included in the series to be studied in the hope that on deprotonation in the alkaline medium it may be possible that rotation about the 1 - 1' bond may be restricted by electronic effects.



VII

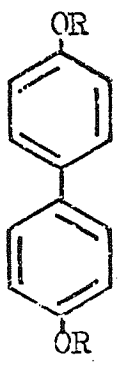


VIII

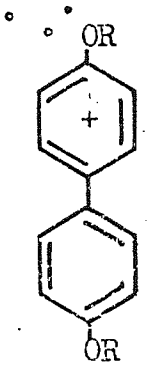
Part III. : Results.

A. Cation Radicals.

The cation radicals studied here were all prepared in 98% concentrated sulphuric acid by methods described previously. A series of compounds was studied in order to notice any continuous or overall group effect. The compounds examined (prac.details in chap.two) were of type IX,



IX



X

where R = H, Me, Et, Ph and p-NO_2Ph.

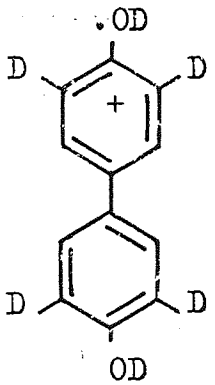
Dissolution of these compounds in 98% concentrated suphuric acid, containing a trace of hydrogen peroxide, leads to the formation of free-radical cations of type X. The results for each compound are given in the order above .

1. Biphenyl-4,4'-diol.

When the required amount of biphenyl-4,4'-diol is added to $2cm^3$ of 98% conc.sulphuric acid, to which a trace of hydrogen peroxide has been previously added, a deep blue paramagnetic solution is produced. The resulting e.s.r.spectrum, 4.1.,

shows seventeen equally spaced lines, due to the diphenosemiquinone cation radical (as in X with R = H). This spectrum is well known (33,34) and arises from the interaction of two groups of four equivalent protons, the values of the splitting constants being 2.05G and 0.71G. On standing, the spectrum changes as progressive sulphonation occurs with the eventual precipitation of biphenyl-4,4'-diol-3,3'-disulphonic acid (33).

When the experiment is repeated using concentrated 98% dideuterated sulphuric acid, the e.s.r.spectrum consists of five equally spaced lines of intensity 1:4:6:4:1, spectrum 4.1.a., and this arises from the hexadeuterated species XI.

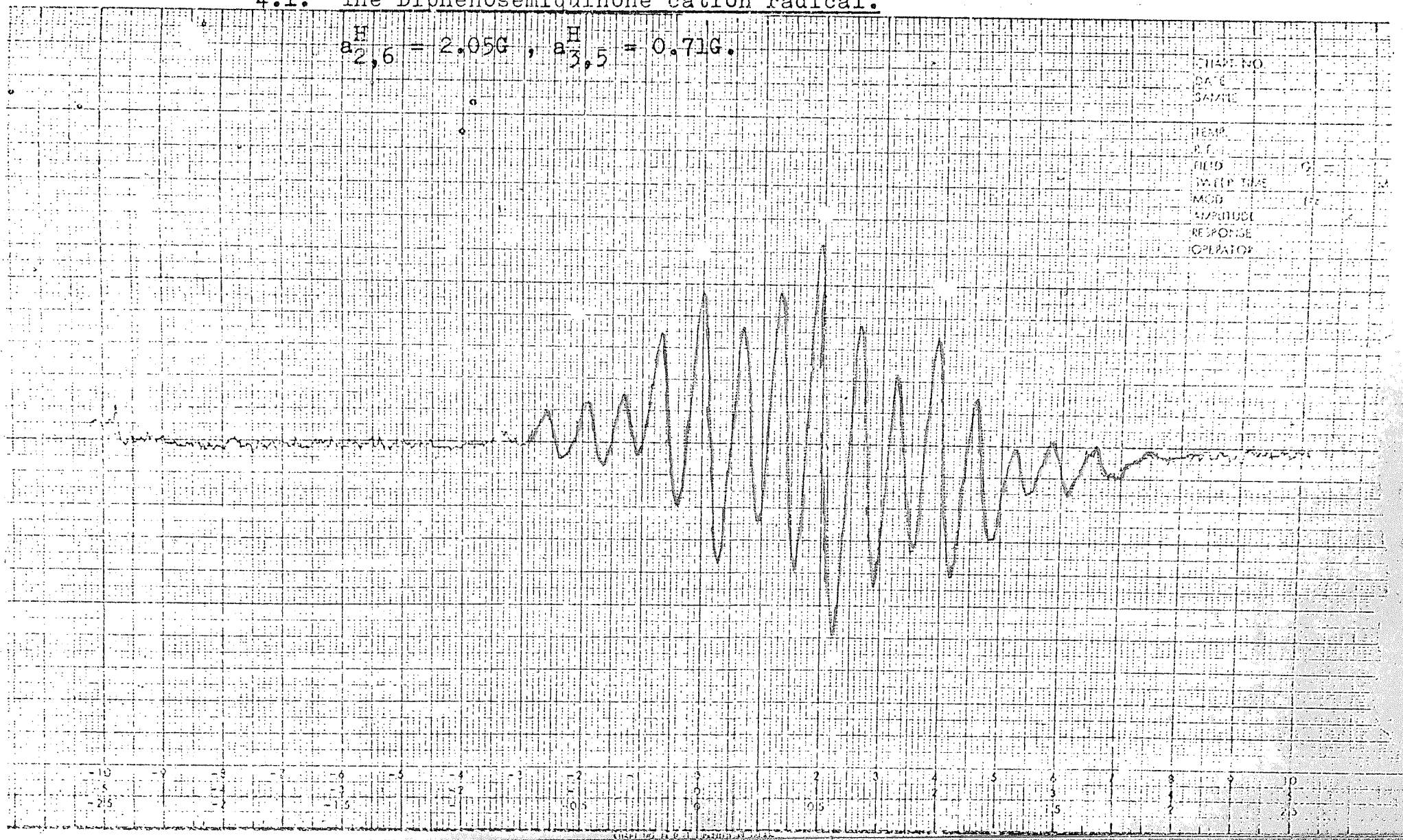


XI

The overall reaction is slow, passing through several stages of progressive deuteration before XI is reached (see chap. six). The reaction serves to show that in diphenosemiquinone cation radicals, the major splitting in their e.s.r.spectra arises from the interaction of the protons in positions 2,6, 2' and 6'. In 4.1.a. the splitting constant is 2.01G, which is identical to the major splitting in 4.1.

4.1. The Diphenosemiquinone cation radical.

$a^{H}_{2,6} = 2.05G$, $a^{H}_{3,5} = 0.71G.$



2. 4,4'-Dimethoxybiphenyl and 4,4'-diethoxybiphenyl.

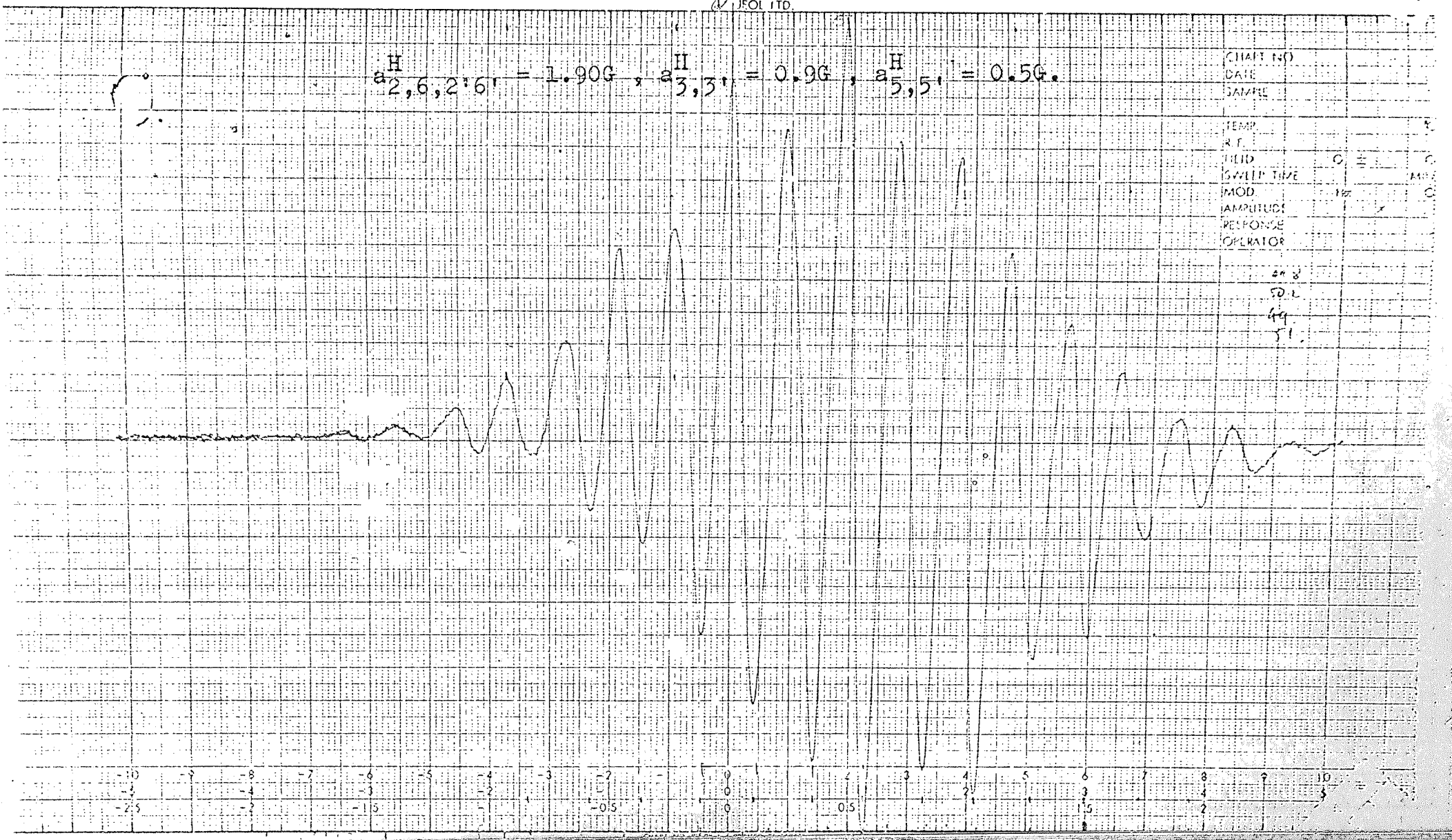
When a little 4,4'-dimethoxybiphenyl is added to concentrated sulphuric acid containing a trace of hydrogen peroxide, a paramagnetic solution giving rise to a nineteen line e.s.r. spectrum is initially produced (spectrum 4.3.). When the diethoxy- compound is subjected to the same conditions, a similar spectrum results (4.4.).

If the instrumental conditions are varied, in this case a reduction in the modulation width by a factor of ten, both spectra show a further degree of hyperfine interaction. This is more noticeable in the 4,4'-dimethoxybiphenyl cation radical (spectrum 4.5.), although the diethoxy- cation does show a considerable change, under similar conditions.

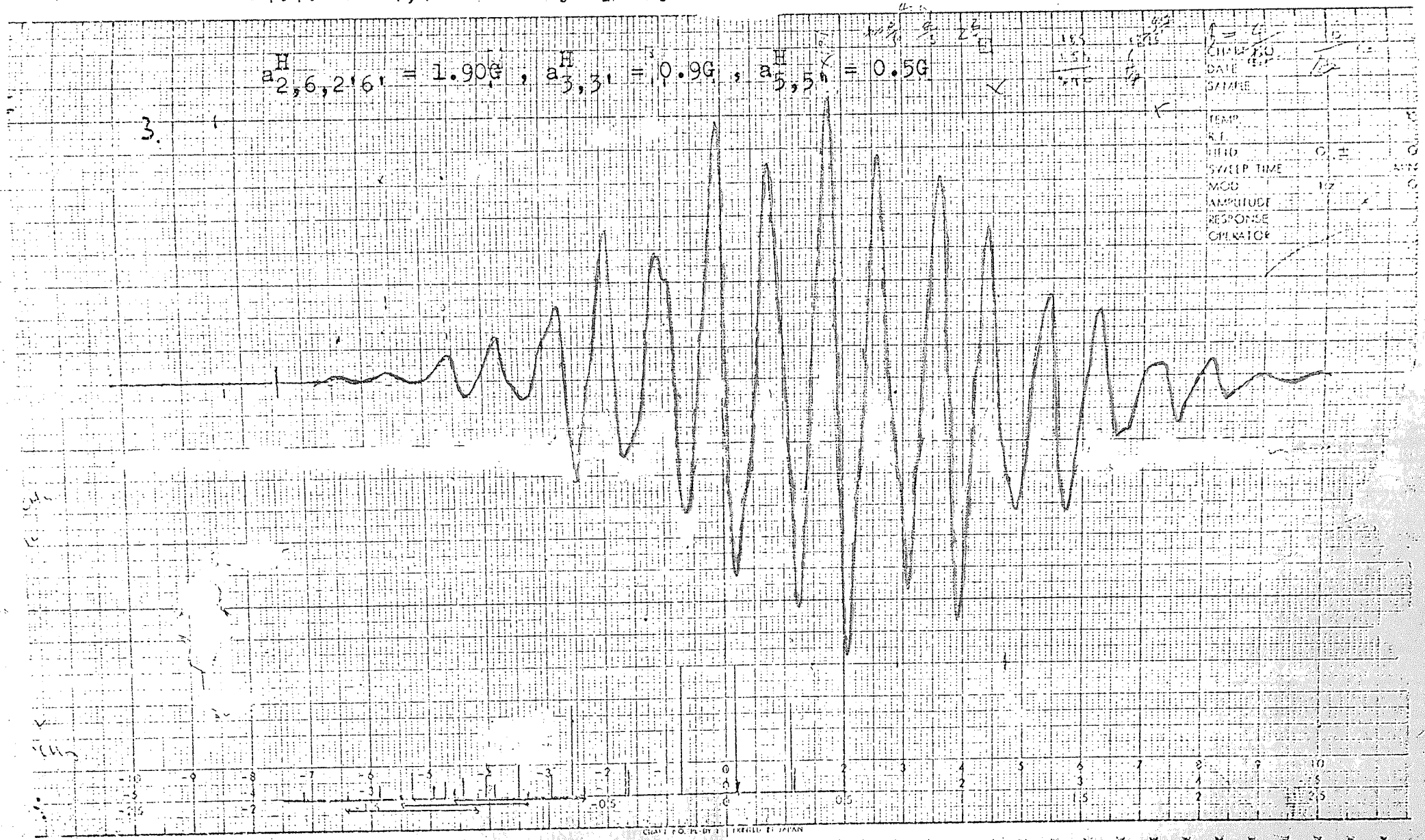
The results seem to suggest that the two initial spectra are derived from the same or similar species, independent of alkyl substituent. The spectra 4.3 and 4.4 can be analysed in terms of the interactions of one group of four equivalent protons having a hyperfine splitting of 1.9G (from the 2,2', 6 and 6' protons), twoequivalent protons having a splitting of 0.9G, and two further protons with a splitting of 0.5 G, these last two values arising from the fact that the position 3 and 3' protons are not equivalent to the 5 and 5' protons, depending on whether they are oriented cis- or trans- with respect to each other.

It is thus recognised that the fine splitting shown in 4.5 of the dimethoxy compound (expanded in 4.5.a and 4.5.b.) is

4. : The 4,4'-Dimethoxybiphenyl cation radical.

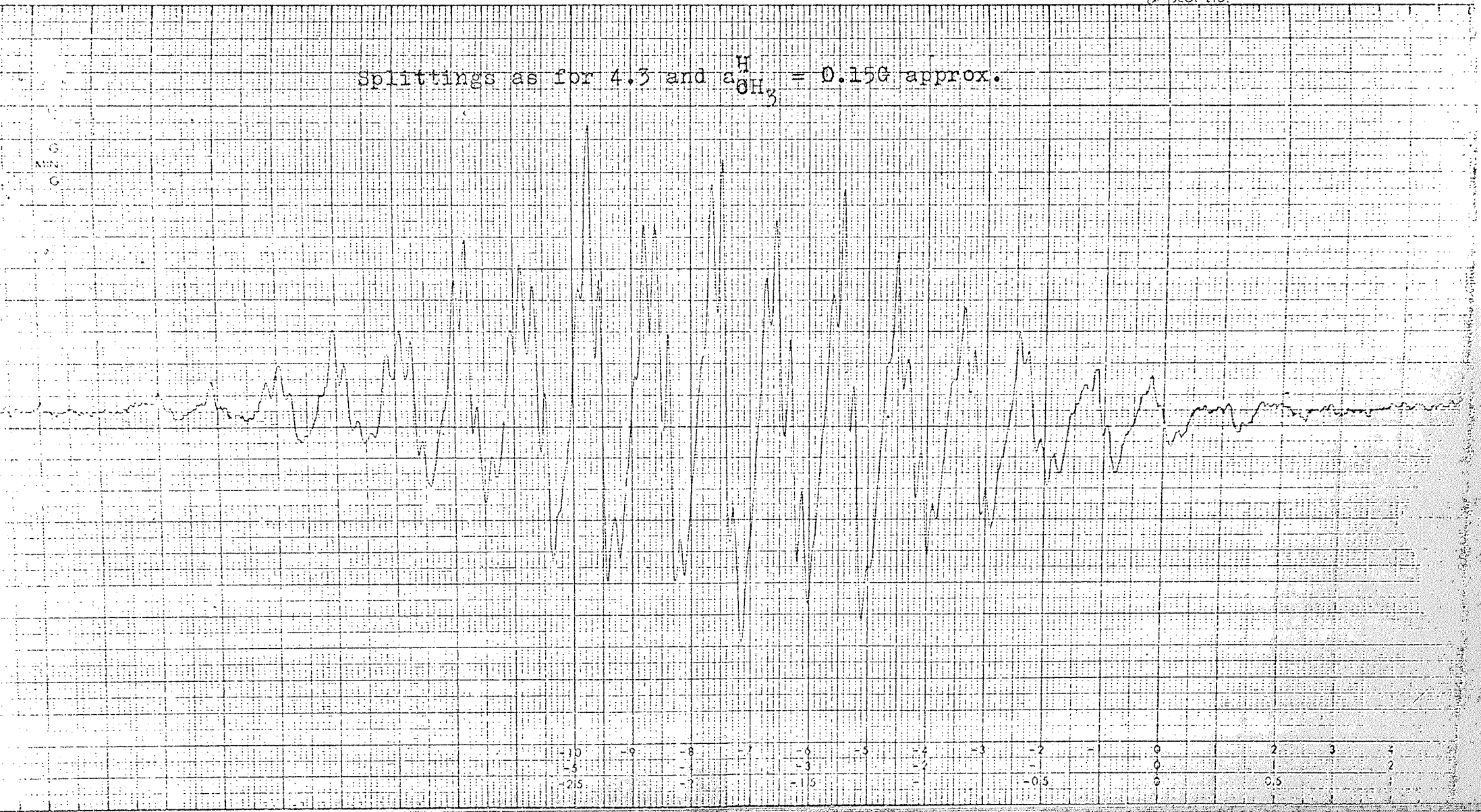


4.4. The 4,4'-Diethoxybiphenyl cation.

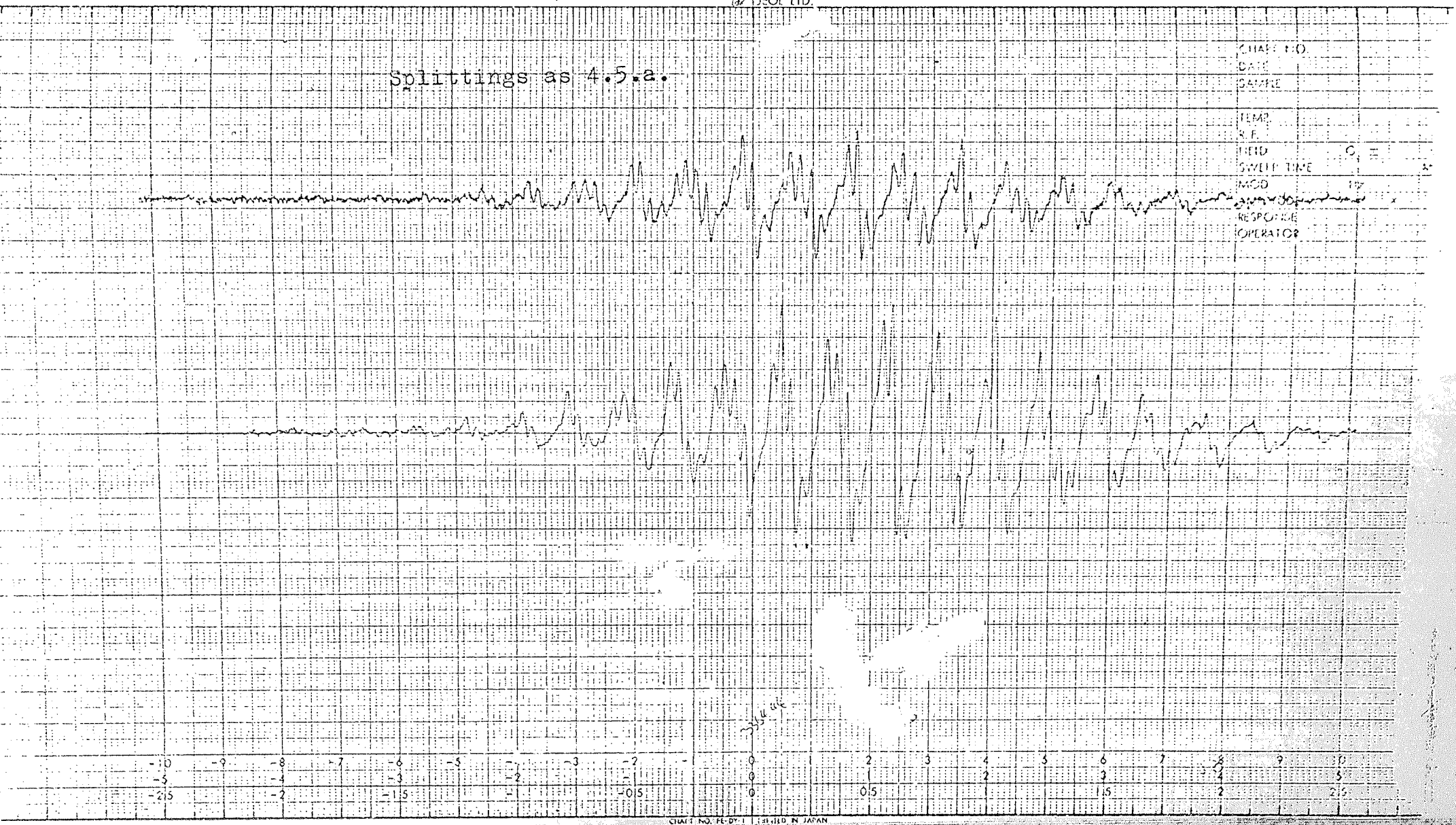


4.5.a. The 4,4'-Dimethoxybiphenyl cation.

Splittings as for 4.3 and $a^{H}_{OCH_3}$ = 0.15G approx.



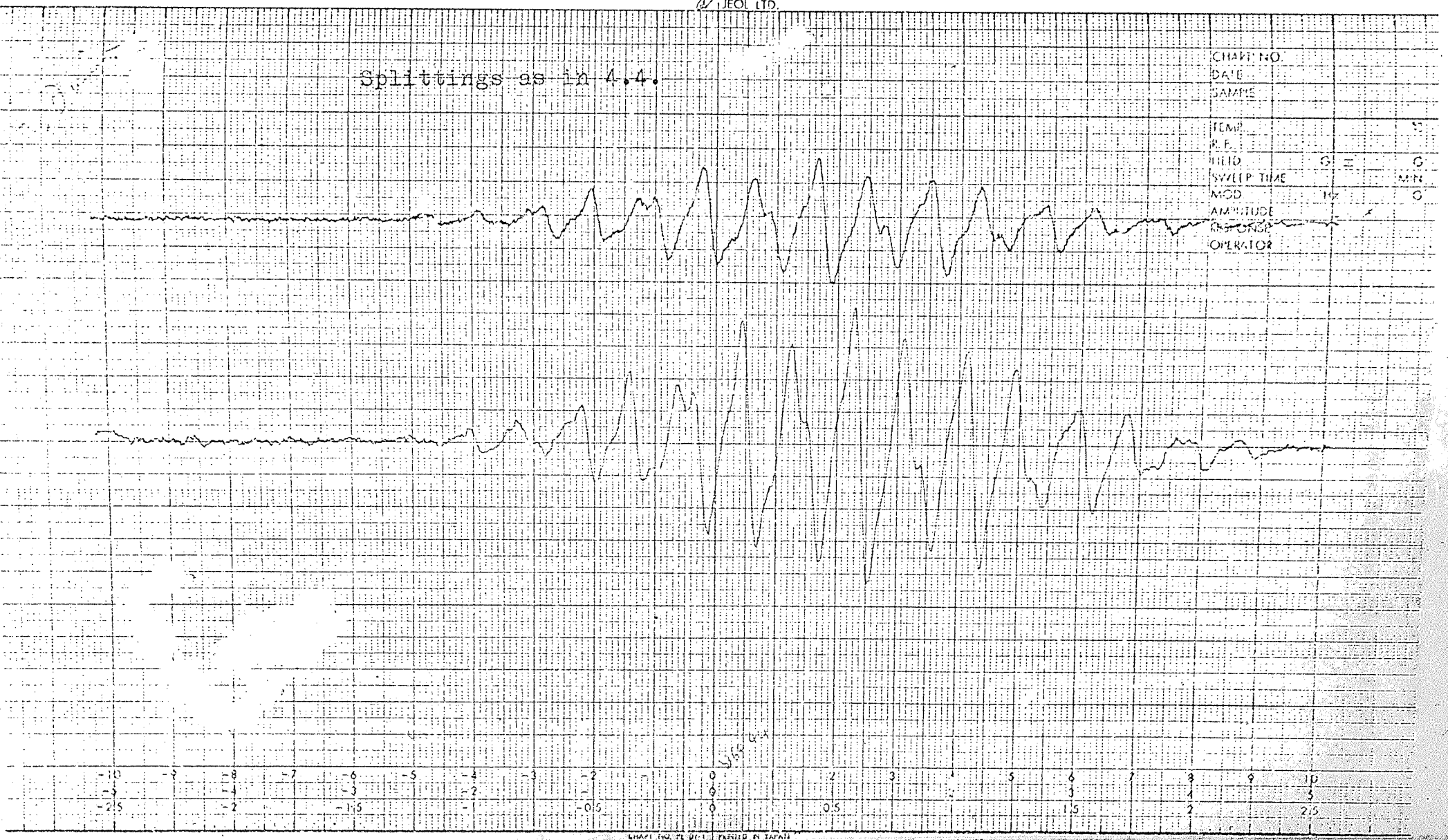
4.5.b. The 4,4'-Dimethoxybiphenyl cation.



Splittings as 4.5.a.

4.6. The 4,4'-Diethoxybiphenyl cation.

Splittings as in 4.4.



due to the further interaction of the methyl group protons (a^{H}_{Me} = 0.15G approx.). These results are discussed in detail later in the chapter.

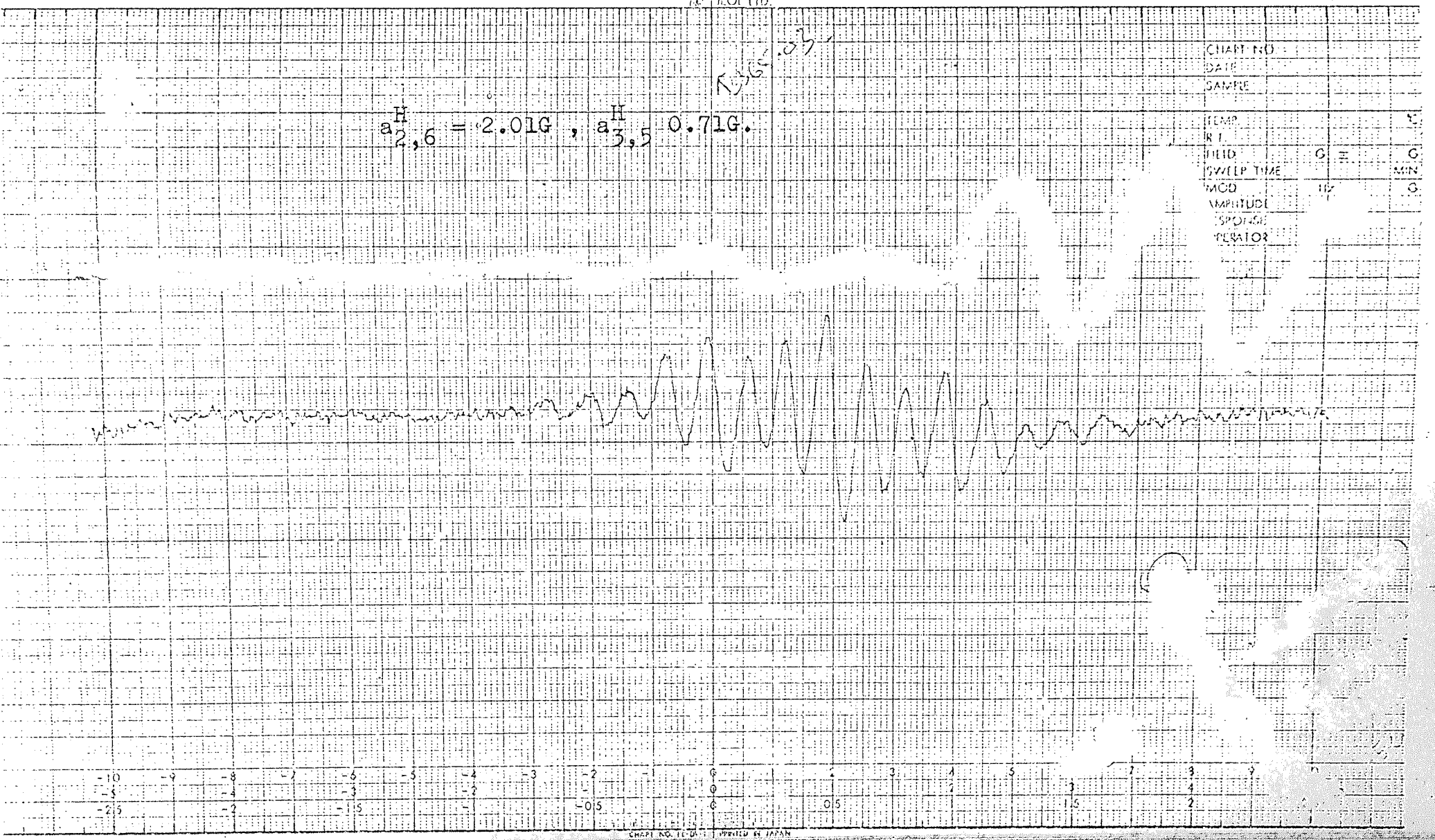
3. 4,4-Diphenoxybiphenyl.

This compound, when added to 98% sulphuric acid containing a trace of oxidising agent, yields a deep blue solution. However, no e.s.r.signal could be detected from the solution under any instrumental conditions.

4. 4,4'-Di(p-nitrophenoxy)biphenyl.

This compound was prepared as described in chapter two and the addition of the requisite amount of it to $2cm^3$ of conc. sulphuric acid containing a trace of hydrogen peroxide gave a blue paramagnetic solution. The e.s.r.spectrum of this solution was found to be identical to that of the dipheno-semiquinone cation radical produced by the oxidation of biphenyl-4,4'-diol. The spectrum of the nitro- compound, 4.7 , consists of seventeen equally spaced lines from the interaction of two groups of four equivalent protons with no interaction from the groups attached to the oxygen atoms.

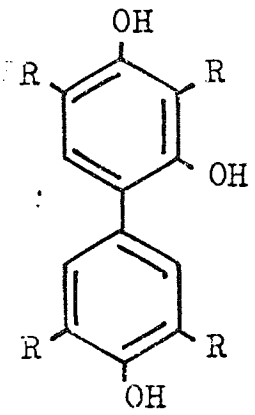
4.7. The 4,4'-Di(p-nitrophenoxy)biphenyl cation



$a^{H}_{2,6} = 2.01G$, $a^{H}_{3,5}$ 0.71G.

B. Anion Radicals.

The anion radicals studied here were all prepared by the air oxidation of the parent compounds, nos.IV, V and VI below, in a solvent mixture of 2M potassium hydroxide and pyridine (1 : 1 by volume).



IV, R = Me,

V, R = OMe;

VI, R = ^{t}Bu.

The preparation of the compounds is described in chapter two.

1. Air Oxidation of 3,3',5,5'-tetramethylbiphenyl-2,4,4'-triol.

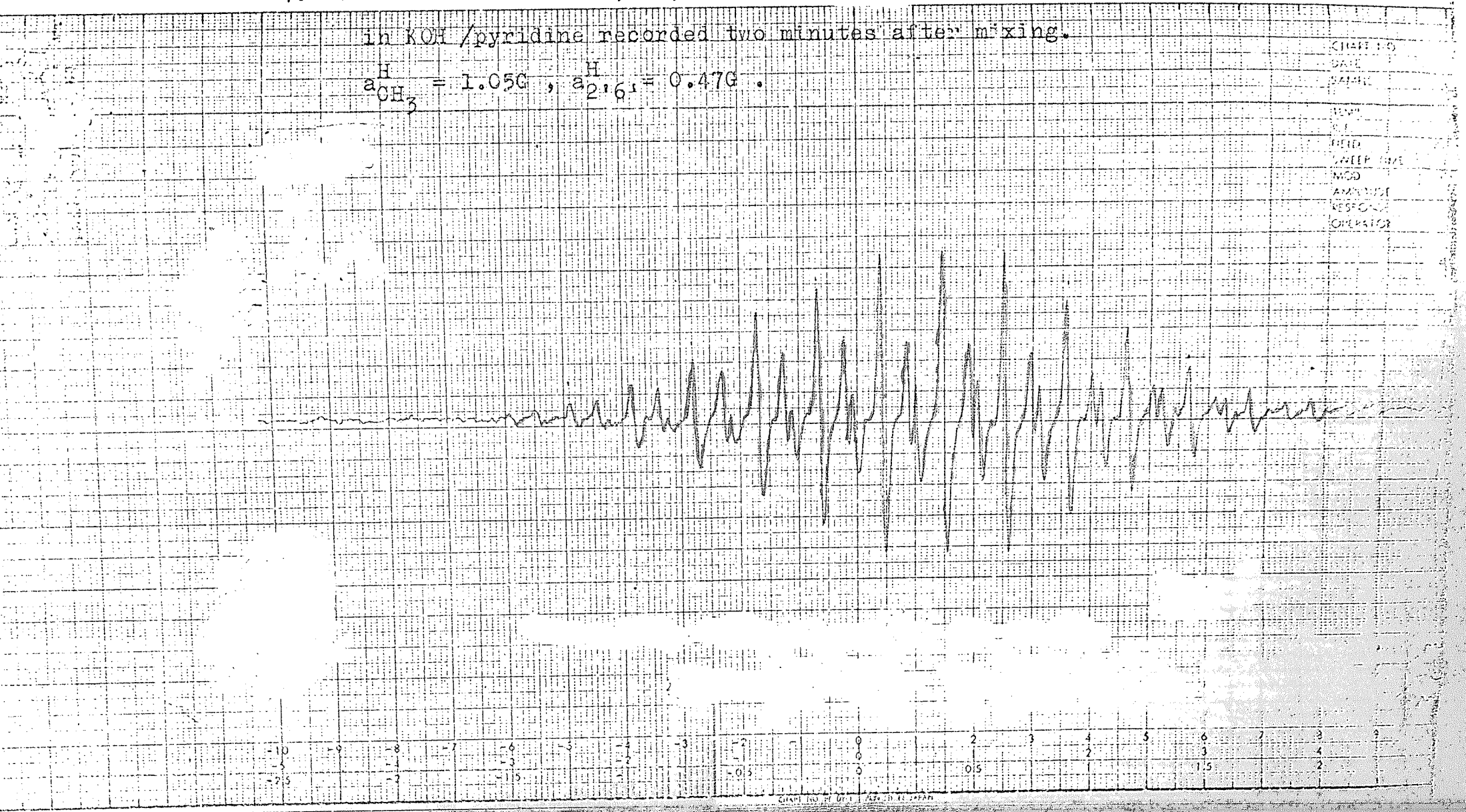
When this compound is oxidised in the solvent mixture of potassium hydroxide and pyridine described above, it yields an orange-brown solution that is paramagnetic and gives the e.s.r.spectrum 4.10. On standing, the spectrum changes, and the final result is spectrum 4.11.

4.10 may be attributed to the interaction of a group of twelve equivalent protons, with each of the thirteen lines produced being further split into triplets by the interaction of a pair of equivalent protons. The radical species involved

4.10. Air oxidation of 3,3'5,5'-Tetramethylbiphenyl-2,4,4'-triol.

in KOH /pyridine recorded two minutes after mixing.

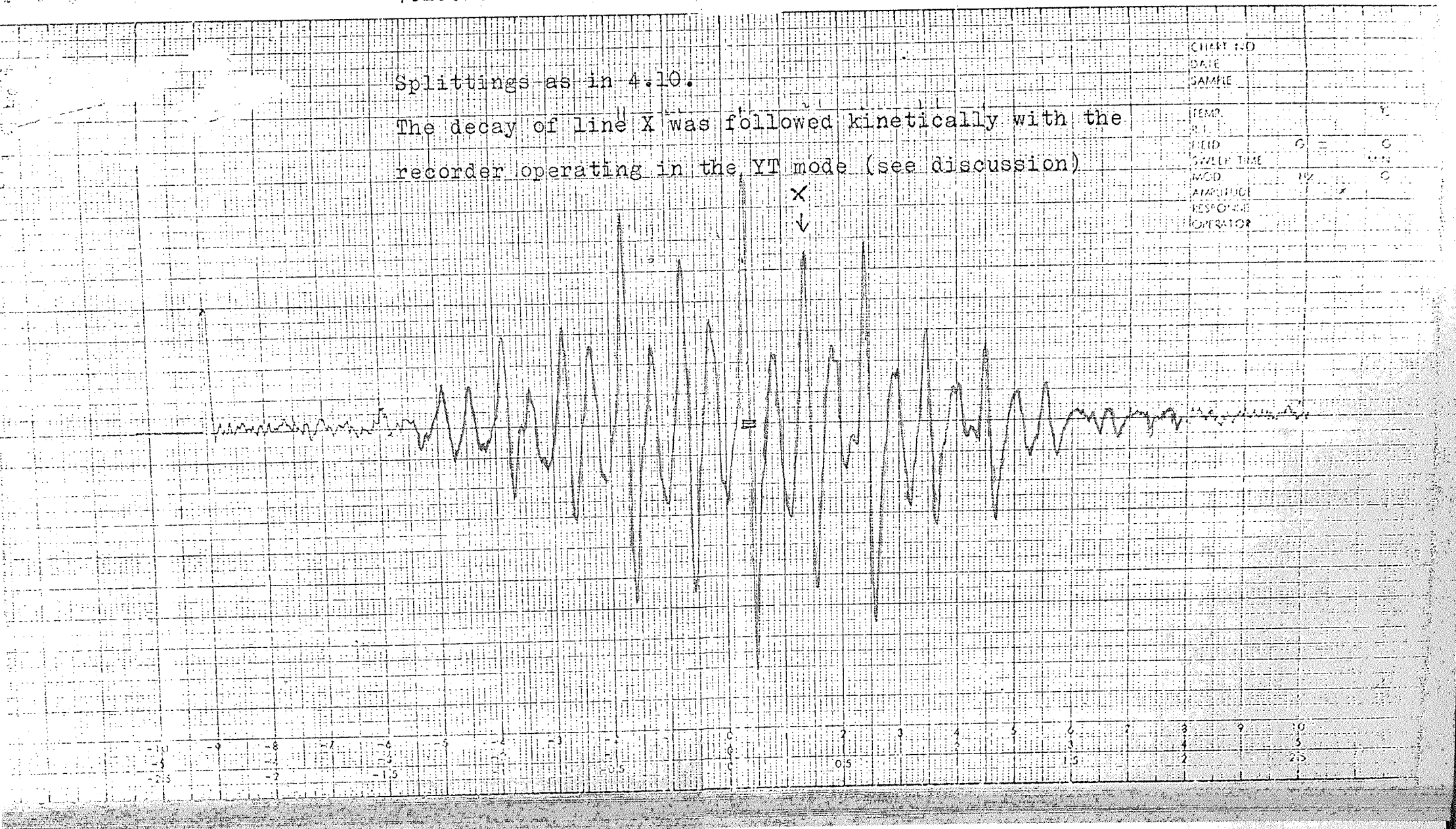
$a^{H}_{CH_3} = 1.05G$, $a^{H}_{2',6'} = 0.47G$.



4.10.b.

Splittings as in 4.10.

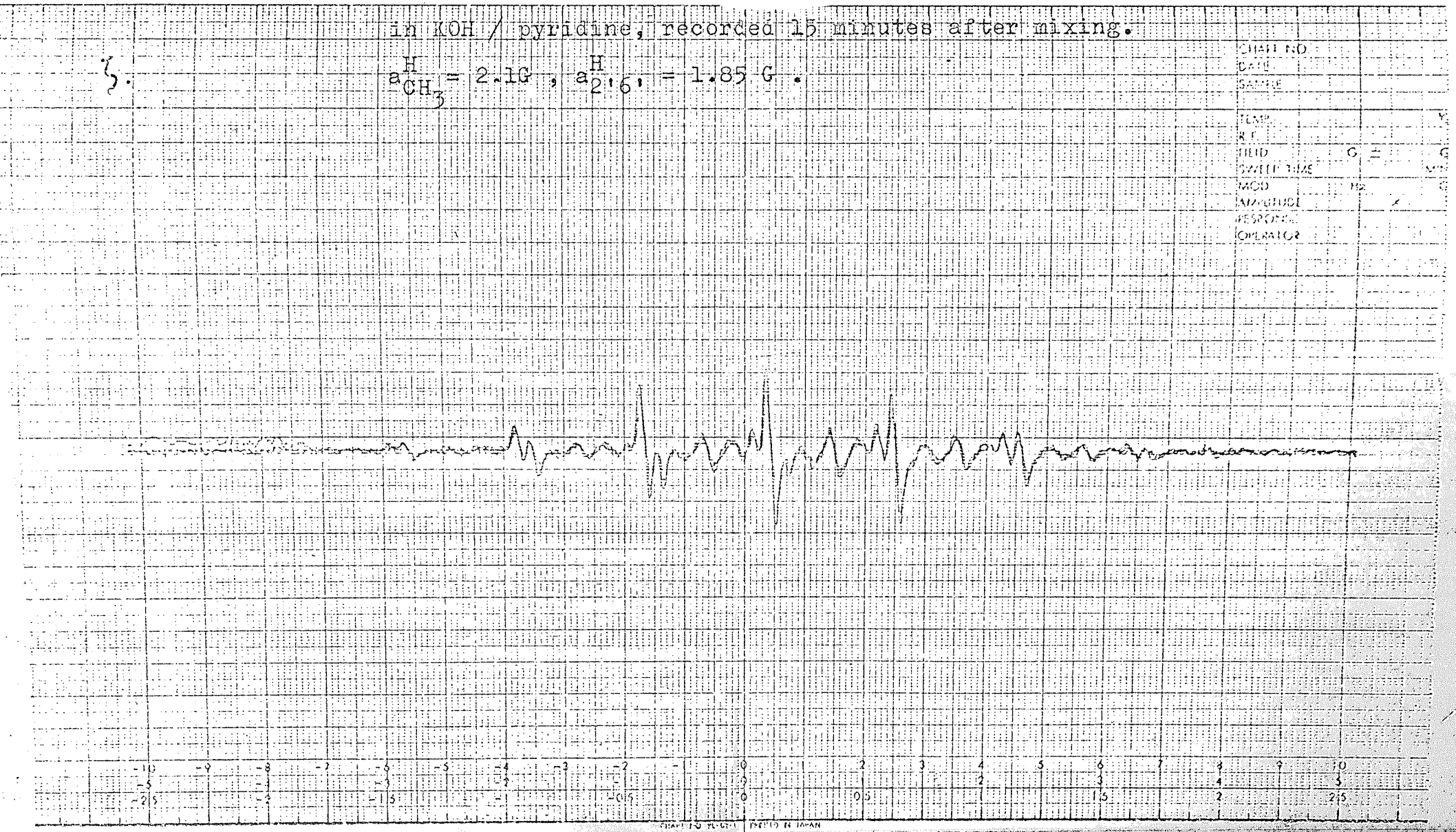
The decay of line X was followed kinetically with the recorder operating in the YT mode (see discussion)



4.11. Air oxidation of 3,3'5,5"-Tetramethylbiphenyl-2,4,4'-triol in KOH / pyridine, recorded 15 minutes after mixing.

ζ.

$a^{H}_{CH_3} = 2.1\,G$, $a^{H}_{2',6'} = 1.85\,G$.

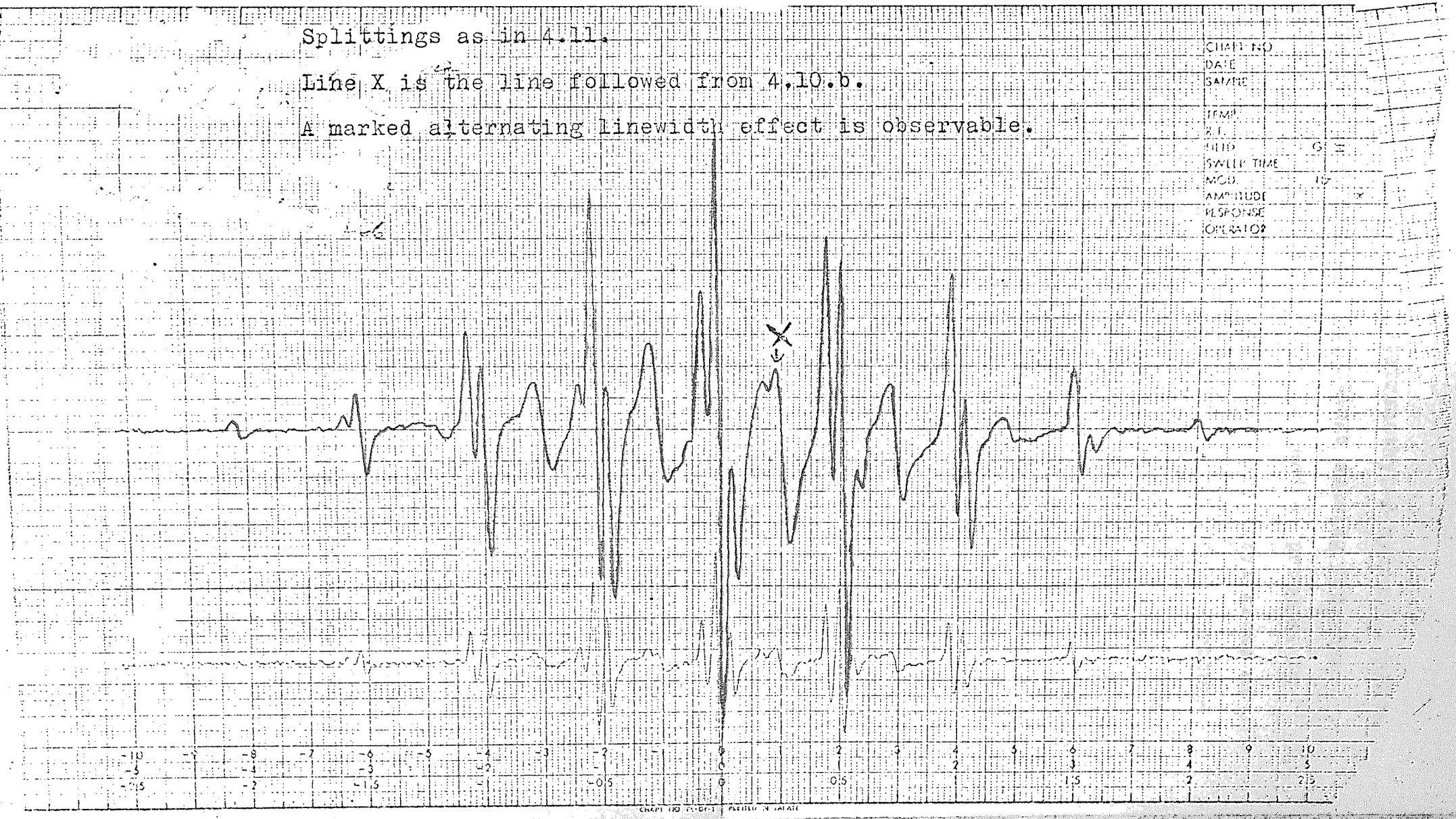


4.11.d.

Splittings as in 4.11.

Line X is the line followed from 4.10.b.

A marked alternating linewidth effect is observable.



is thought to be the 3,3',5,5'-tetramethyl-2-hydroxydiphenosemiquinone anion, the major splittings arising from the twelve methyl group protons and the 2' and 6' protons. It is thought that the deprotonation of the hydroxyl group at position 2 may be slow, with the result that when deprotonation is affected, 4.11 is formed. 4.11 clearly arises from the interaction of a group of six equivalent protons with a group of two equivalent protons causing the further splitting. The values of the hyperfine splittings observed in both spectra are as follows.

4.10., a^{H}_{Me} = 1.05G, $a^{H}_{2;6'}$ = 0.47G,

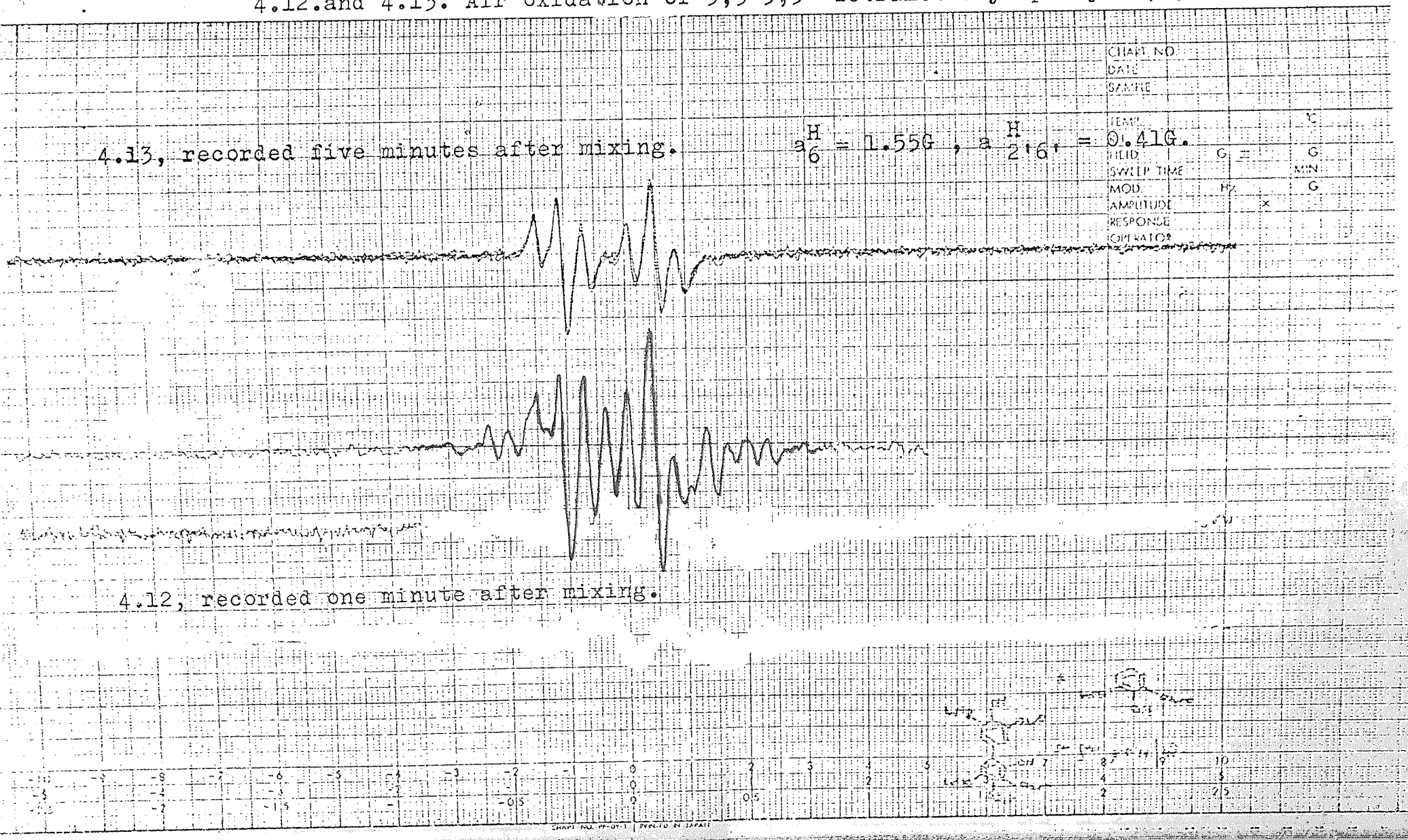
4.11, a^{H}_{Me} = 2.1G, $a^{H}_{2;6'}$ = 1.85G.

2. Oxidation of 3,3',5,5'-tetramethoxybiphenyl-2,4,4'-triol and 3,3',5,5'-tetra-tert-butylbiphenyl-2,4,4'-triol.

Both these compounds give a paramagnetic solution when a little of either is dissolved in $1cm^3$ of 2M potassium hydroxide / pyridine solvent.

The former compound initially gives spectrum 4.12, but this changes rapidly to yield the spectrum4.13. 4.12 is complex and difficult to rationalise but the final result, 4.13 is a simple six line spectrum consisting of a pair of lines (a = 1.55G) each split into triplets (a = 0.4G) by a group of two equivalent protons. It is thought that the major splitting arises from the position 6 proton, further split by the interaction of the 2' and 6' protons.

4.12.and 4.13. Air oxidation of 3,3'5,5'-Tetramethoxybiphenyl-2,4,4'-triol.

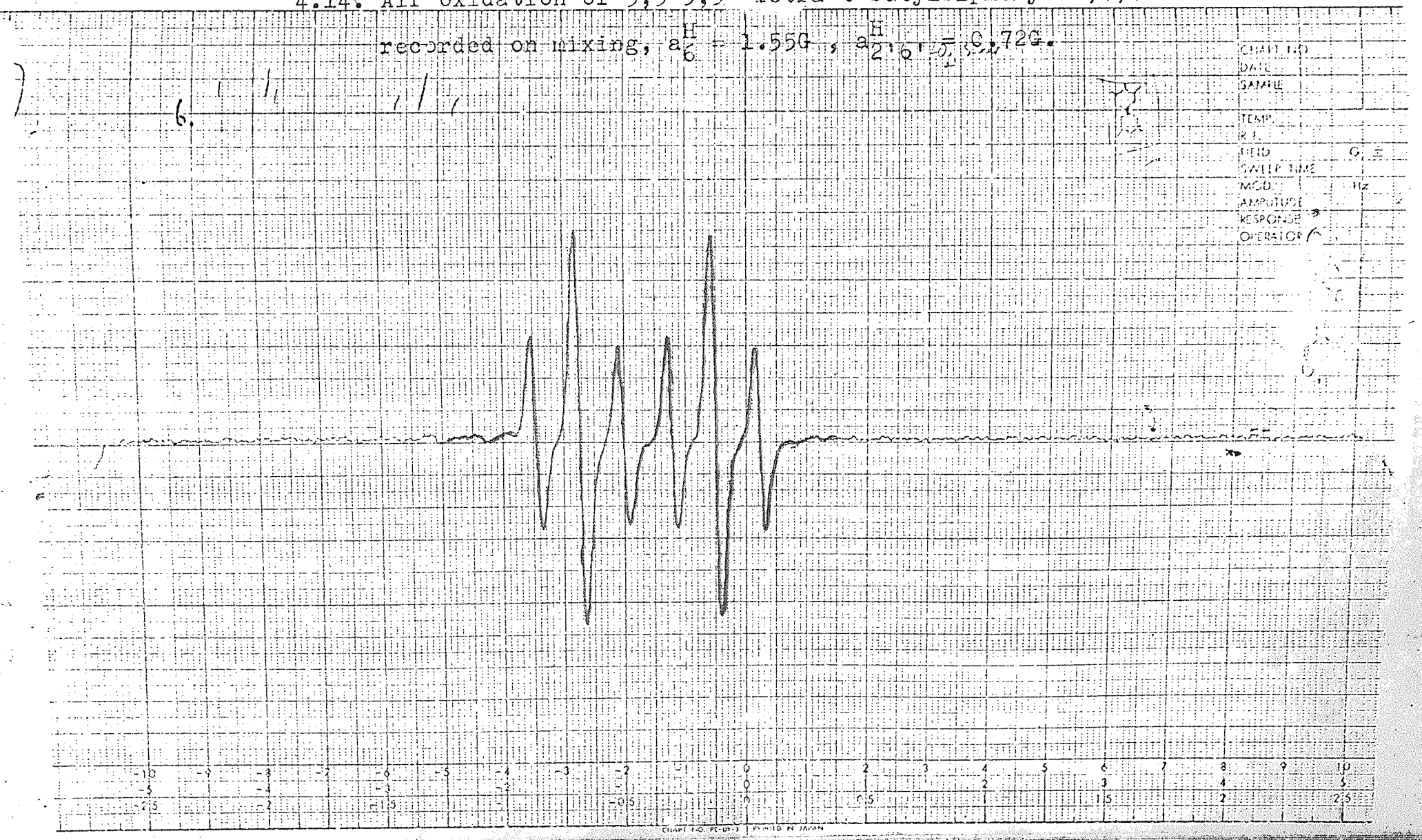


4.13, recorded five minutes after mixing. $a^{H}_{6} = 1.55G$, $a^{H}_{2'6'} = 0.41G.$

4.12, recorded one minute after mixing.

4.14. Air oxidation of 3,3'5,5'-Tetra-t-butylbiphenyl-2,4,4'-triol.

recorded on mixing, $a^{H}_{6'}$ = 1.55G, $a^{H}_{2',6'}$ = 0.72G.



The spectrum of the tetra-t-butyl- radical is obtained on mixing, and is similar to 4.13. This spectrum is thought to arise from the interactions of the same protons involved in 4.13 with the difference that in this case 4.14, the values of the splittings are larger (a^{H}_{5} = 1.55G , $a^{H}_{2;6'}$ = 0.7G.).

3. Air oxidation of 2,2',4,4'-tetrahydroxybiphenyl.

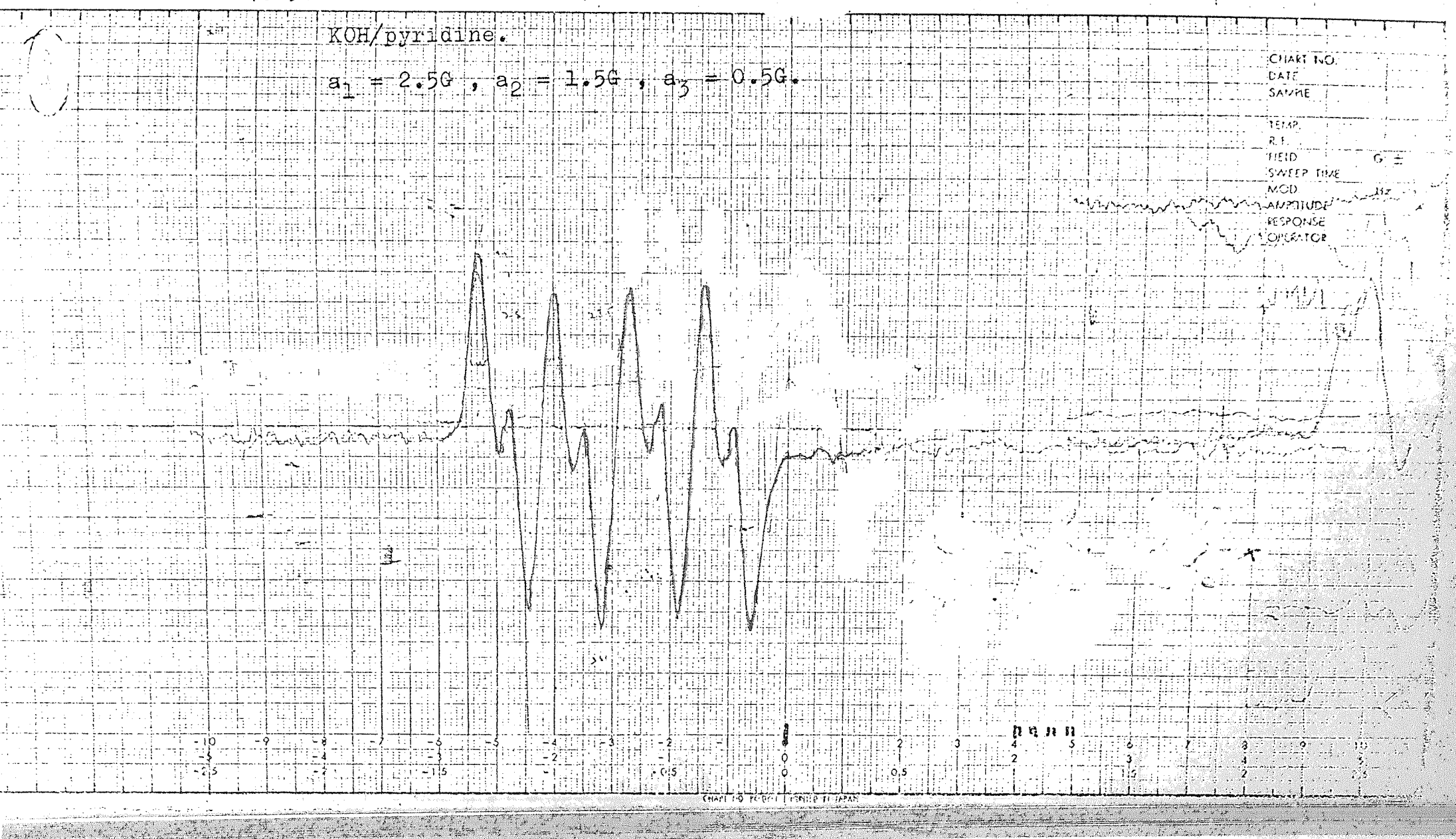
When a little of this compound is added to $1cm^3$ of solvent, a pale brown paramagnetic solution is obtained. The e.s.r. spectrum arising from this solution is recorded in 4.14, which consists of four equally spaced doublets of equal intensity. The eight line spectrum is assigned to the interaction of three single non-equivalent protons, the hyperfine splittings arising from each being 2.5G, 1.5G and 0.5G.

The species producing this spectrum is thought to be a diradical dianion of type XII. This might arise if the two oxygen atoms at positions 2 and 2' carried the negative charges after deprotonation, and orientating themselves as far apart as possible, fixing the 1 - 1' bond and enabling the hydroxyl groups at 4 and 4' to be oxidised independently without any interaction of the free electrons across the 1 - 1' bond.

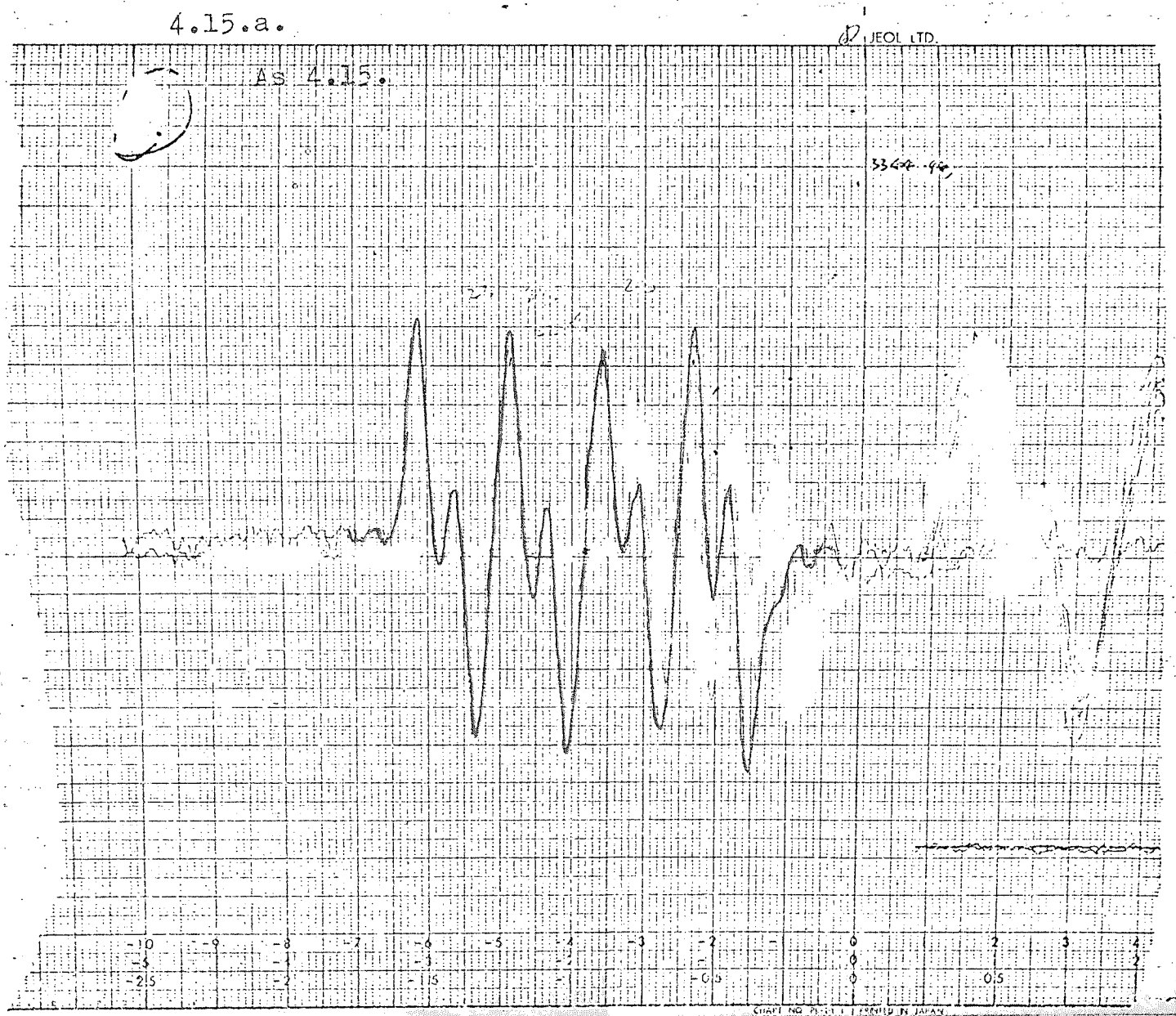
4.15. Air oxidation of 2,2'4,4'-Tetrahydroxybiphenyl.

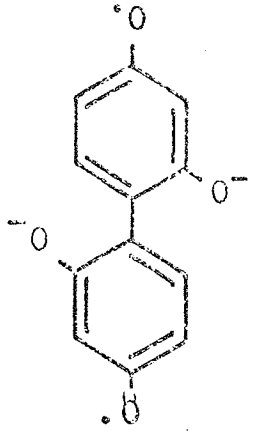
KOH/pyridine.

$a_1 = 2.5G$, $a_2 = 1.5G$, $a_3 = 0.5G$.



4.15.a.





XII

Part IV - Discussion

A. Cation Radicals

1. Introduction

When studying the cation radicals of 4,4'-dimethoxybiphenyl and 4,4'-diethoxybiphenyl in sulphuric acid, using the Hilger and Watts 'Microspin' X-band spectrometer (chap.2), it was noted that the general shape and appearance of the spectra were similar to that of the diphenosemiquinone cation, and this may have indicated the occurrance of dealkylation reactions. It was decided that the reactions warranted further study, but as quantitative measurements on the spectrometer were difficult due to the comparitively low sensitivity, a more detailed examination was precluded at that time. The increased resolution of the JEOL spectrometer, and the ease with which quantitative measurements could be made, facilitatde the further study of these compounds. In addition, two more compounds were prepared, the diphenoxy- and di(p-nitrophenoxy)- analogues, this latter example with a view to inducing dearylation to occur, aided by the electron withdrawing properties of the p-nitro- group.

The results obtained from the experiments require both the alternating linewidth effect and some simple molecular orbital considerations to be taken into account.

2. The Mechanism of Methyl Group Proton Hyperfine Splittings in Conjugated Systems.

It is well known that in cyclic, fully conjugated π-electron systems, it is possible for methyl group proton hyperfine splittings to be as great or greater than the ring proton splittings in the same π-electron system. Some values for methyl substituted diphenosemiquinone radicals are tabulated in figure 4.c.

Diphenosemiquinone radical	a^H_{Me}	a^H_{ring}	ref.
3,3',5,5'-tetra-Me- anion	1.85G	0.54G	32.
3,3',5,5'-tetra-OMe- anion	0.49G	0.49G	31.
3,3'-dimethyl- anion	1.96G	a^H_2 0.48G a^H_6 0.78G a^H_5 2.36G	38.
3,3'-di-Me-5,5'-di-^{t}Bu- anion	2.00G	a^H_2 0.56G a^H_6 0.42G (a)	38.

(a),- no splitting from the t-butyl protons.

4.c.

The mechanism which effectively couples the methyl group protons to the π-electron system is known as 'hyperconjugation'. This mechanism makes use of the fact that the interaction between two parts of a molecule may be increased if the symmetries of the wave functions of the fragments are the same.

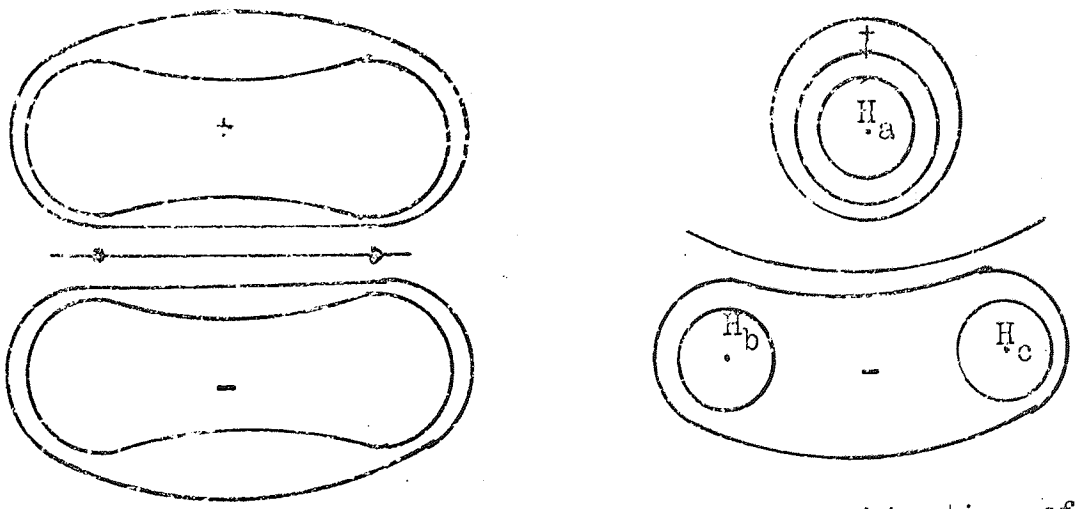
A π-orbital changes its sign upon reflection in the molecular plane. It is thus assymetric with respect to that plane. It is possible to combine the atomic orbitals of three hydrogen atoms to give a molecular orbital, similarly asymmetric as a π-orbital. If the wave functions of the atomic orbitals of the three hydrogen atoms are ϕ_1, ϕ_2 and ϕ_3, permitted linear combinations of these are,

$$\Psi = c_1\phi_1 + c_2(\phi_2 + \phi_3)$$

$$\Psi = c_1(\phi_1 + \phi_2) + c_2\phi_3$$

and $$\Psi = c_1(\phi_1 + \phi_3) + c_2\phi_2.$$

Diagrammatically, the similarity between any of these combinations and a simple π-orbital (formed by a linear combination of two $2p_z$ orbitals) can be shown as in 4. .



a. simple π-orbital b. linear combination of three proton atomic orbitals

Fig. 4.d.

b.may be considered as a 'pseudo' π-orbital, and may thus be regarded as part of the conjugated π-electron system. So we can say that where methyl group proton hyperfine

splittings are larger than expected (or larger than the ring proton splitting in the same molecule), this is due to the direct coupling of the methyl protons to the π-electron system.

Further to the initial concept of hyperconjugation, experiments establishing the sign of the spin density at the methyl group carbon atom and the magnitude and sign of the splittings of the methyl protons relative to each other, are now well known (77,78).

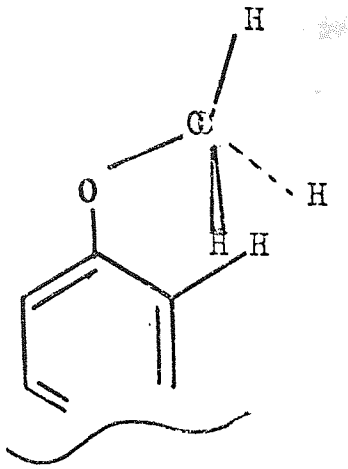
3. The e.s.r.Spectra of the 4,4'-Dimethoxybiphenyl and 4,4'-Diethoxybiphenyl Cation Radicals.

Sullivan (79,80) has examined the spectra of these cation radicals in an aluminium chloride / nitromethane solvent system. His analysis shows that the major hyperfine splittings in the spectra are derived from the alkyl group protons, thus requiring the hyperconjugative effect to be present in both examples. However, it is evident for a number of reasons that when 98% concentrated sulphuric acid is used as the solvent medium that this is not the case. In the analyses of the spectra obtained in these experiments, the alkyl proton splitting is thought to be the least important interaction in both examples, and no alkyl group proton splitting can be discerned in the case of the 4,4'-diethoxybiphenyl cation.

A comparison of alkyl substituted semiquinone cations and the corresponding anions shows in general that, while the

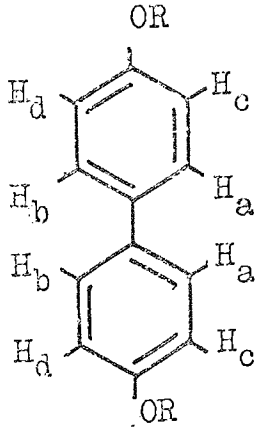
methyl proton splitting is often larger than the ring proton splitting in the anion radical. In the corresponding cation the methyl proton splitting is decreased and is much less significant. A relevant example is that of the 3,3',5,5'-tetramethyldiphenosemiquinone radical : the anion has a methyl proton splitting of 1.85G and a ring proton value of 0.54G (32); the corresponding values for the cation are 0.54G and 1.96G respectively(33). Another example is that of the 3,3',5,5'tetra-sec-butyldiphenosemiquinone radical : the splitting constant of the methin proton of the anion and cation (ineach case the methin and ring protons give an equivalent interaction) being 0.78G and 0.23G respectivley (see this work chapters five and six). These results lead us to believe that the coupling of the alkyl group protons to the π-electron system in diphenosemiquinone cations through hyperconjugation is decreased sufficiently to cause a considerable decrease in the splitting constants of the alkyl protons.

In addition, in the case of the 4,4'-dimethoxybiphenyl cation, the case for the hyperconjugation of the methyl group protons may be dismissed on steric grounds. Dreiding type, and other models of the compound show that the methyl group is fixed and cannot rotate. The methyl group is fixed with one hydrogen atom in the molecular plane, with the other two straddling the C_3 - H bond as in diagram 4.e., withthe result that any combination of the three hydrogen atomic orbitals cannot give a pseudo π-orbital that is similarly symmetric to the molecular π-orbital.



4.e.

Considering the alternating linewidth effect as discussed earlier, it is reasonable to assume that, if the interaction of the methyl group is small and completely free rotation about the C_4 - O bond was occurring, then the resulting e.s.r.spectrum would be identical to that of the diphenosemiquinone cation radical. That it is not is indicative of the fact that rotation is fixed. As a result, the spectrum may be expected to arise from the interactions of four groups of two equivalent protons (4.f)



4.f.

In practice, the nineteen line spectra initially produced from the compounds where R is Me and Et can be attributed to the interactions of one group of four equivalent protons giving the major splitting (the 2,2;6,6' protons) and two groups of two equivalent protons giving the smaller splittings (the protons H_a and H_b in 4.6).

An assignment for the splittings of $a^H_{2,2;6,6'} = 1.86G$, $a^H_{H_a} = 0.9G$ and $a^H_{H_b} = 0.49G$ (these last two values are for the 3,3'and 5,5' pairs of protons),would yield an e.s.r.spectrum of twenty-three lines, the centre nineteen lines being identical to spectra 4.3 and4.4 (the outer two lines of the spectra being too small to be detected). This interpretation would also give a value of 10.00G for the spectral extent, and this is similar to that for the dipheno-semiquinone cation radical (spectral extent 10.01G, see spectrum 4.1.). The alternating linewidth effect, when observed in any radical species shows that, irrespective of the process involved (rotation, inversion etc.)being at fast, slow or intermediate rates of exchange, the spectral extent remains unaltered. The results obtained here agree with this interpretation well.

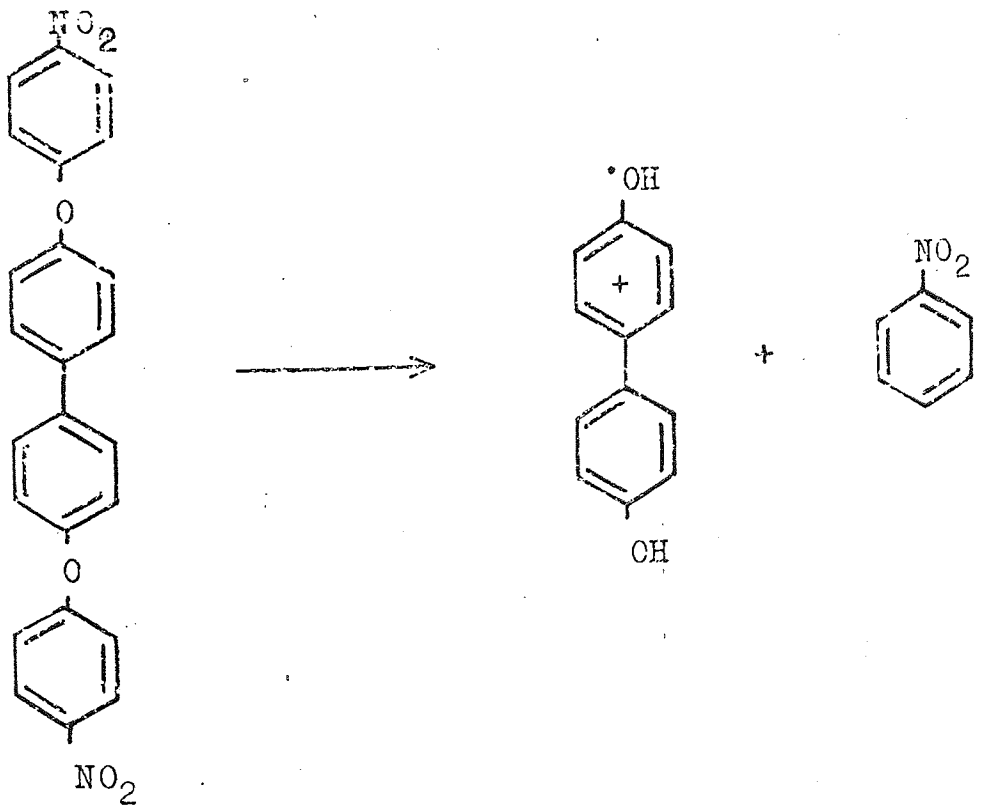
In the case of the 4,4'-dimethoxybiphenyl cation, further splitting is observed due to the methyl group proton inter-action (see spectra 4.5.a, and 4.5.b.). The exact values of the splittings are difficult to determine, but are about 0.16G. It can be expected that there are two splittings arising from the six methyl group protons. Because the methyl group is fixed (see figure4.5), four of the protons

are equivalent (those not in the molecular plane), and the other two protons form another equivalent group.

4, 4,4'-Di(p-nitrophenoxy)biphenyl.

In this example it appears that a straightforward dearylation reaction is taking place, to give the diphenosemiquinone cation radical (giving spectrum 4.7), the other product possibly being nitrobenzene.

The effect of the p-nitro- group in the aryl substituent is to withdraw electrons from the conjugated π-electron system through the $C_4 - O - C_4(Ar)$ system causing an increase of negative charge on the oxygen atom. This would allow electrophilic attack by hydrogen ions from the acidic medium at this position, yielding the diphenosemiquinone cation radical.

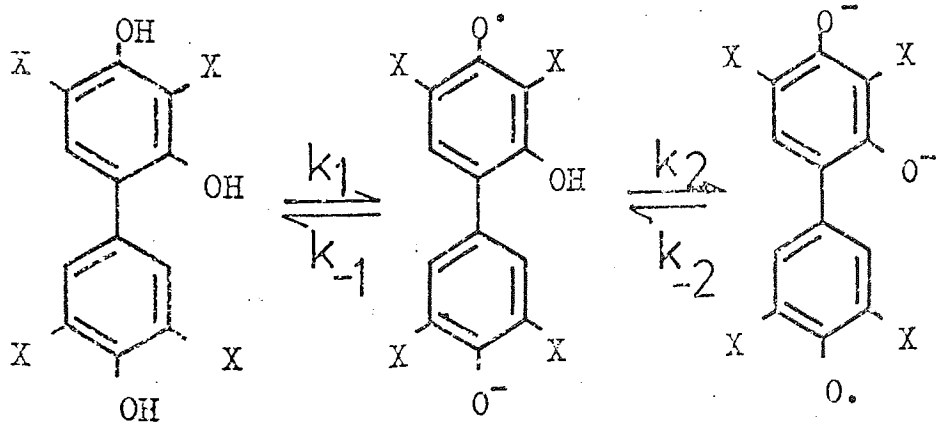


B. Anion Radicals.

1. Radicals Derived from
3,3'5,5'-Tetraalkyl-2,4,4'-trihydroxybiphenyls.

When the e.s.r.measurements obtained from anion radicals of these compounds (see this chap.part II.B.compounds IV,V,VI.) are compared with those of the corresponding tetraalkyl-diphenosemiquinone anions, striking differences are observed. These differences are due, not unexpectedly, to the presence of the hydroxyl group at position 2, and its effect on the delocalised π-electron system of the diphenosemiquinones after deprotonation in the alkaline medium. It would appear from the results that, despite the alkaline reaction medium, that the positon 2 hydroxyl group has acidic properties and that the rate of its deprotonation is fundamental in determining the shape of the e.s.r.spectra.

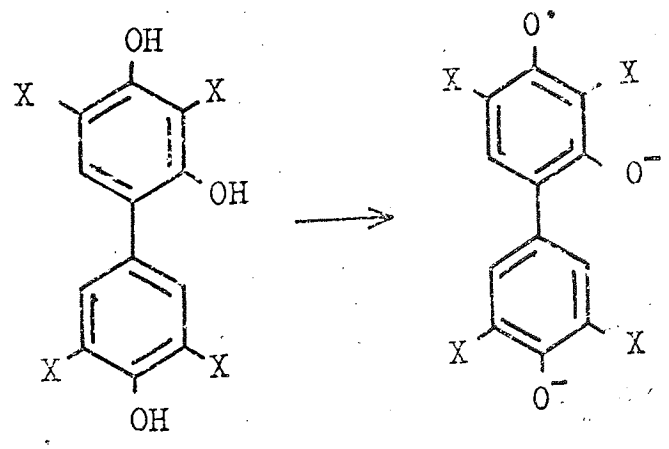
From the evidence obtained here, it would appear that a reaction as in figure 4.h.is occurring



4.h.

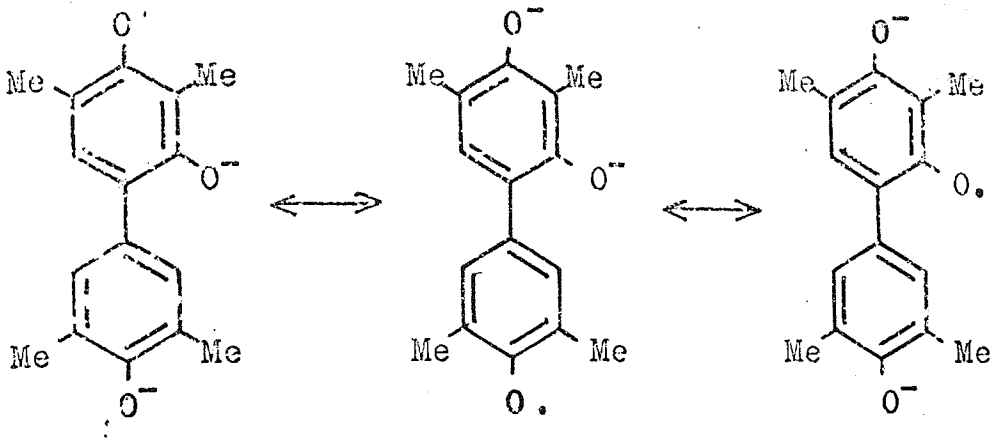
with k_1 being fast and then k_2 being the overall rate determining step, depending on the acidity of the hydroxyl proton in XVI. This is borne out by the fact that all the compounds examined produced spectra on mixing with the pyridine /potassium hydroxide solvent. The tetramethyl compound gave a spectrum which changed over ten minutes to give another simple spectrum (4.10 - 4.11) while the tetramethoxy-compound also gave an initially complex spectrum which again changed to one much simpler, but more rapidly than the tetramethyl- analogue (4.12 - 4.13), but the tetrabutyl- compuond gave a simple six line spectrum on mixing (4.14), which remained unchanged. These results are consistent with k_2 being rate determining. If it is assumed that k_2 is dependent on the acidity of the position 2 hydroxyl group, then k_2 is expected to increase for the series R = Me → R = OMe → R = ^{t}Bu as the acidity of the hydroxyl group proton decreases (a series of 2,4-di-R-phenols has a series of pk_a values of R = H > Me > OMe > ^{t}Bu).

If the deprotonation of the hydroxyl group at position 2 was rapid , then a reaction such as in figure 4.i would occur.



4.i.

this maybe discounted however, because in the case of the tetramethyl compound the second spectrum, formed after ten minutes exhibits the alternating linewidth effect partially due to resonance forms thus,



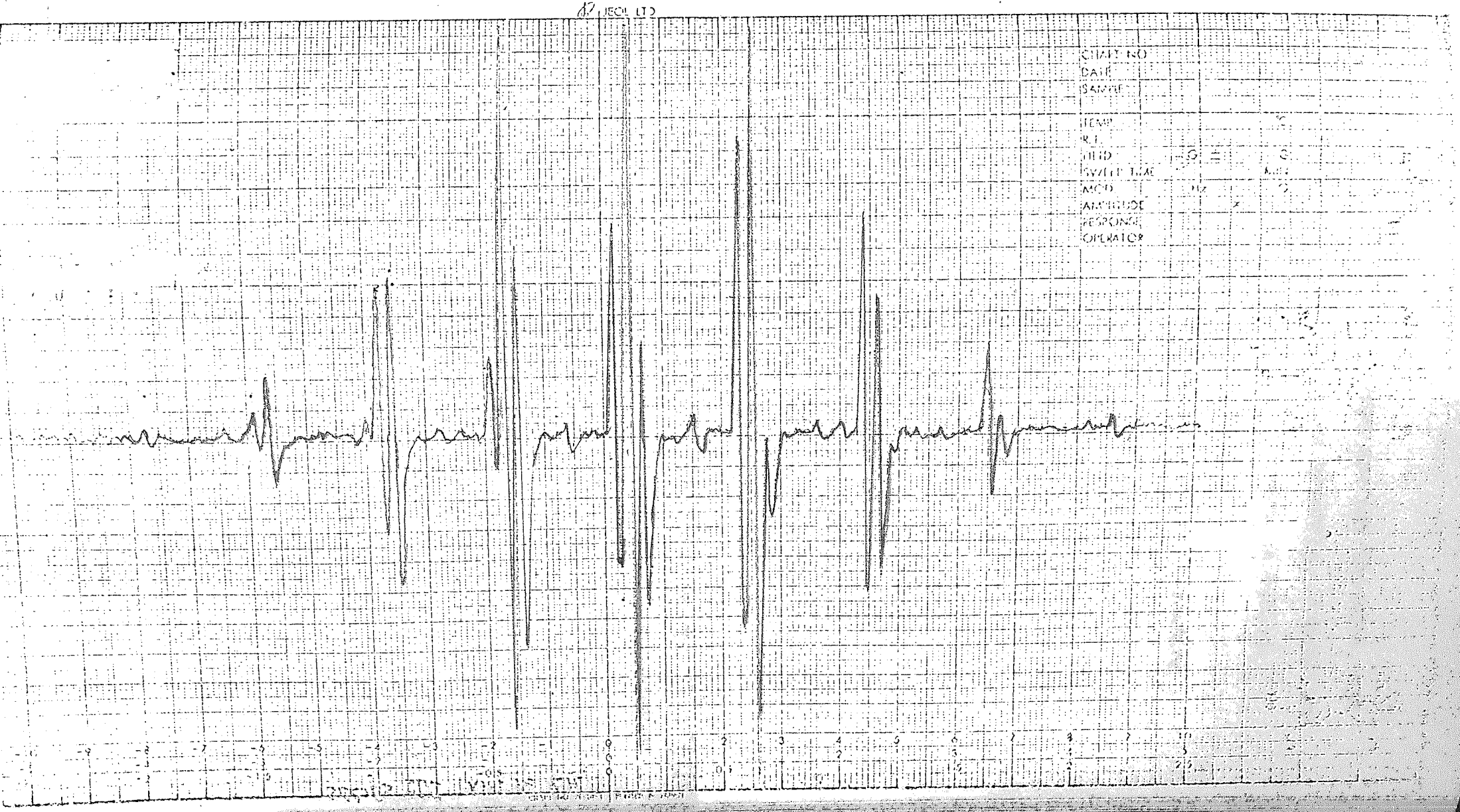
XX XXI XXII

so if the deprotonation at position 2 occurred on mixing, the initial spectrum should exhibit the alternating linewidth effect.

The alternating linewidth effect observable in the tetramethyl compound may arise from either or from a combination of the two processes now described.

Firstly, a species such as XX above may give rise to the observation of an alternating linewidth effect if rotation about the 1 - 1' bond were not fast. If rotation about the 1 - 1' bond were fast an e.s.r.spectrum with a major splitting arising from twelve equivalent protons would result (similar to 4.10), there being complete delocalisation of the free electron throughout the π -electron system. If on the other hand, the 1 - 1' bond were fixed, then a spectrum similar to that for 2,6-dimethylbenzosemiquinone would be expected, as in

4.16. The 2,6-dimethylbenzosemiquinone anion.



spectra appear similar, the splittings are not the same, and 4.11 quite clearly shows a more complex hyperfine interaction from the intermediate lines, especially clear in 4.11 d.

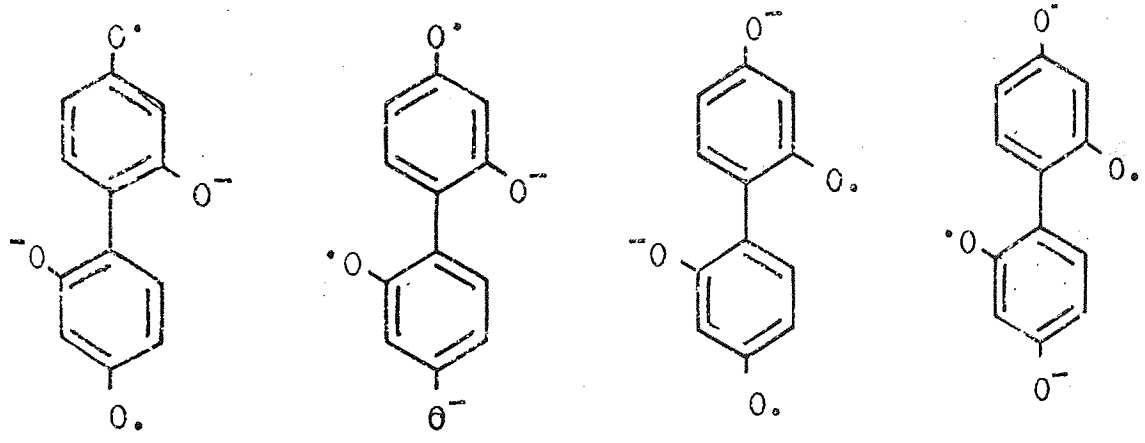
The second mechanism that may give rise to an alternating linewidth effect is the deprotonation of the position 2 hydroxyl group to give resonance forms of type XX, XXI and XXII above. In this system, no contribution is expected from XXII, as in this case all the splittings would be different and thus spectra arising from it would be complex. It is likely that the rate of interchange between XX and XXI is slow with the equilibrium being shifted to XXI. This is borne out experimentally by the fact that the rate of disappearance of one line in spectrum 4.10.b.(marked X), was followed using the YT recorder (described in chap.2.II), and although the line decreased in intensity significantly, as in figure 4.j., it was always observable in the final spectrum (4.11.d - after deprotonation). In 4.j the build up of XVI is followed to a maximum and the concentration of the protonated species then declines rapidly to give XX/XXI .

The actual mechanism causing the alternating linewidth effect in the tetramethyl compound is probably a combination of the two processes with XXI being the favoured resonance configuration and also rotation about the 1 - 1' bond is restricted with the favoured orientation of the two rings with respect to each other being that where the oxygen atom at position 2 (carrying the negative charge) is perpendicular to the plane of the 2'and 6'protons (enabling them to appear

equivalent as spectrum 4.11)

In the tetramethoxy- and tetra-tert-butyl- compounds, the resonance figures analogous to XX and XXI must have an equilibrium favouring forms of the type XX, while rotation about the 1 - 1' bond must be unrestricted, there being no observable alternating linewidth effect. Thus, with species of type XX being favoured, the position 6 proton has the major splitting, while there is an equivalent interaction from the 2' and 6' protons.

From the spectrum obtained by the oxidation of 2,2',4,4'-tetrahydroxybiphenyl, an anion diradical is the only logical explanation of the results, such a species might be stabilised by resonance forms of the type in figure 4.k, and exchange between each of them being fast averages out any non-equivalence of the protons giving the splittings. The 1 - 1' bond must be fixed all the time otherwise a more complex splitting pattern would arise if there were any interaction at all across it.

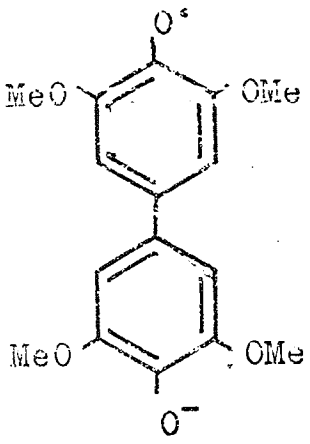


CHAPTER FIVE

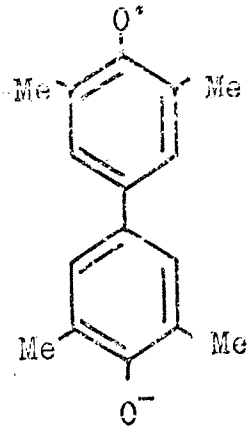
DIPHENOSEMIQUINONE ANION RADICALS.

Part I : Previous Studies.

While studying alkoxy derivatives of semiquinone anions by e.s.r.spectroscopy, Matsunaga and MacDowell (31) prepared the 3,3',5,5'-tetramethyl- and 3,3',5,5'-tetramethoxydiphenoquinone semiquinone anion radicals, by the air oxidation of the corresponding biphenyl-4,4'-diols, in a solvent mixture of potassium hydroxide and pyridine (1 : 1 by volume)



I



II

The observed thirteen line spectrum of the methoxy- derivative (I) was explained by assigning a hyperfine coupling constant of 0.49G to both sets of equivalent protons, with two lines at each end of the spectrum being too low in intensity to be detected.

The spectrum from the tetramethyl compound was of twenty one equally spaced lines. Initially, values of 2.34G for the ring protons and 0.78G for the methyl group protons were

the assigned coupling constants. Later studies (32) showed that these results disagreed with the theoretical predictions (given by a simple LCAO/MO method) that the unpaired electron density on carbon atom 3 is at least 1.5 times greater than that on carbon atom 2. An alternative assignment was therefore made for the splittings, these being 1.56G for the methyl protons and 0.78G for the ring protons (this assignment requiring eight lines, four at each end of the spectrum, being too low in intensity to be detected).

Petranek, Pilar and Ryba (38) studied the oxidation and reduction properties of alkyl substituted polynuclear phenols by electrochemical methods. Radical anions produced by the electrochemical reduction of 4,4'-diphenoquinone and some of its derivatives were detected by e.s.r.spectroscopy using fast flow techniques with acetonitrile as solvent.

Having observed large discrepencies in the values of the hyperfine coupling constants of the methyl group protons and the ring protons for the 3,3',5,5'-tetramethyldiphenosemiquinone anion when produced by :

a), air oxidation of the diol (a^{H}_{Me}= 1.56G, a^{H}_{ring}= 0.78G)

b), electrochemical reduction of the quinone (a^{H}_{Me}= 1.88G, a^{H}_{ring}= 0.54G),

a subsequent study by Wheway (34) led to the reexamination of the work of Matsunaga, but extending it to include other alkyl substituted derivatives of diphenoquinone.

The hyperfine coupling constants of the tetramethyldiphenosemiquinone anion were found to vary with the solvent mixture composition. Extensive studies using a variety of

solvent mixtures, including pyridine/KOH, 2-picoline/KOH, acetonitrile/KOH etc., were carried out. The solvent effect theory of Gendell, Freed and Fraenkel (81) when applied to these examples showed that changes in coupling constants between solvated and unsolvated anions of tetramethyldiphenosemiquinone agree with qualitative molecular orbital predictions and that not all alkylated diphenosemiquinone anions exhibit this solvent effect.

Part II : Present Work.

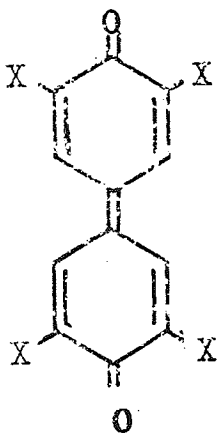
It has been found in this work that diphenosemiquinone anion radicals may be produced when a little of the quinone under study is dissolved in the pyridine/potassium hydroxide solvent mixture mentioned earlier, i.e. the radical is produced by the reduction of the quinone and not by the air oxidation of the corresponding biphenyl-4,4'-diol in the same solvent. This result is consistent with those of Michaelis and Granick (82), who found that phenanthrenequinone could be partially reduced in alkaline solution, the resulting semiquinone anion radical being in equilibrium with its diamagnetic dimer. Furthermore, the dimerisation was suppressed by the addition of an organic solvent such as pyridine.

Selected 3,3',5,5'-tetraalkyldiphenosemiquinone anions were prepared by this method and the resulting e.s.r.spectra were compared with previous measurements (34) in order to note any disagreement, due to the difference in the method of propagation.

3,3'-Dimethylbiphenyl-4,4'-diol was oxidised in the pyridine /potassium hydroxide solvent mixture to give the corresponding diphenosemiquinone anion radical, previously unprepared by chemical methods. The hyperfine coupling constants differ greatly from those reported for the same radical, prepared by the electrochemical reduction of the quinone (38).

Part III : Results.

A. Reduction of Alkylated Diphenoquinones.



III

Compounds as in figure III were prepared as described in chapter two, where X = methyl, iso-propyl, tert-butyl, sec-butyl and methoxy-. The semiquinone radical anions of these compounds were produced by dissolving a little of the quinone in the pyridine /potassium hydroxide solvent mixture. Paramagnetic solutions were produced from the compounds where X = methyl, iso-propyl, sec butyl, and methoxy.

1. The 3,3',5,5'-tetramethyldiphenosemiquinone anion.

This free-radical, prepared as above gave e.s.r.spectra nos. 5.1, 5.2, and 5.3 each produced in a different solvent mixture. The insets in spectrum 5.1 show the wings of the main spectrum under conditions of increased modulation width. The hyperfine splittings and solvent mixtures are shown in table 5.a.

Spec.No.	Solvent mixture comp. (% KOH : % pyridine)	a^{H}_{Me}	a^{H}_{ring}
5.1	63 : 37	1.62	0.85
5.2	50 : 50	1.70	0.74
5.3	38 : 62	1.75	0.69

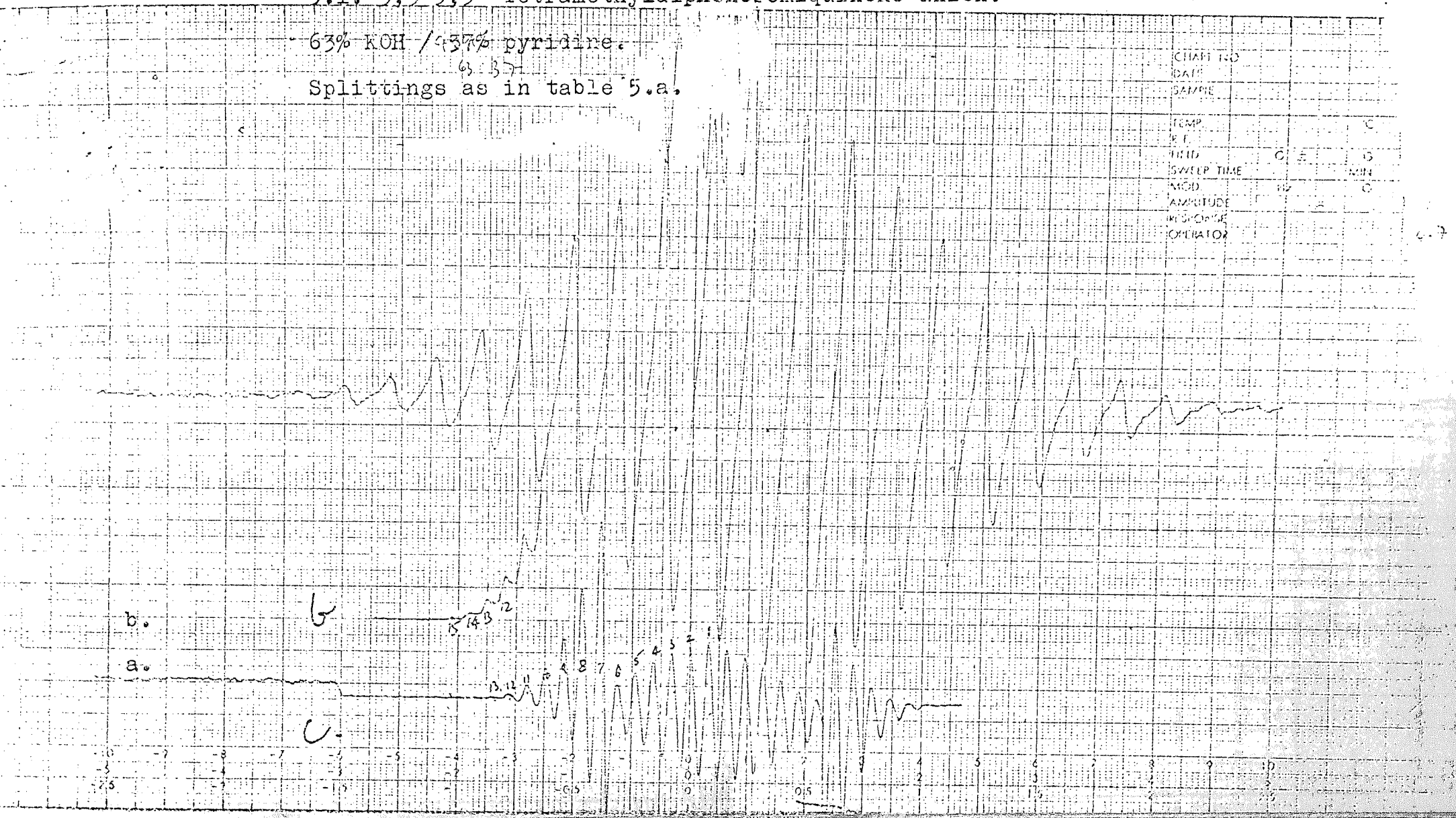
5.a.

Comparisons between these results and those reported for the same radical produced by the air oxidation of the corresponding biphenyl-4,4'-diol are favourable, in showing a similar decrease in the values of a^{H}_{ring} as the proportion of pyridine in the solvent mixture is increased. The insets show the wings of the spectrum in 5.1, and the lines that have been previously unobserved can be clearly seen and are marked. This information yields the first conclusive results showing that the analysis of Matsunaga (32) is correct. If despite the molecular orbital predictions his first analysis had been correct (31) then a twenty-five line spectrum would have resulted. The observation of the previously undetected lines in this case is a good example

5.1. 3,3'5,5'-Tetramethyldiphenosemiquinone anion.

63% KOH / 37% pyridine.

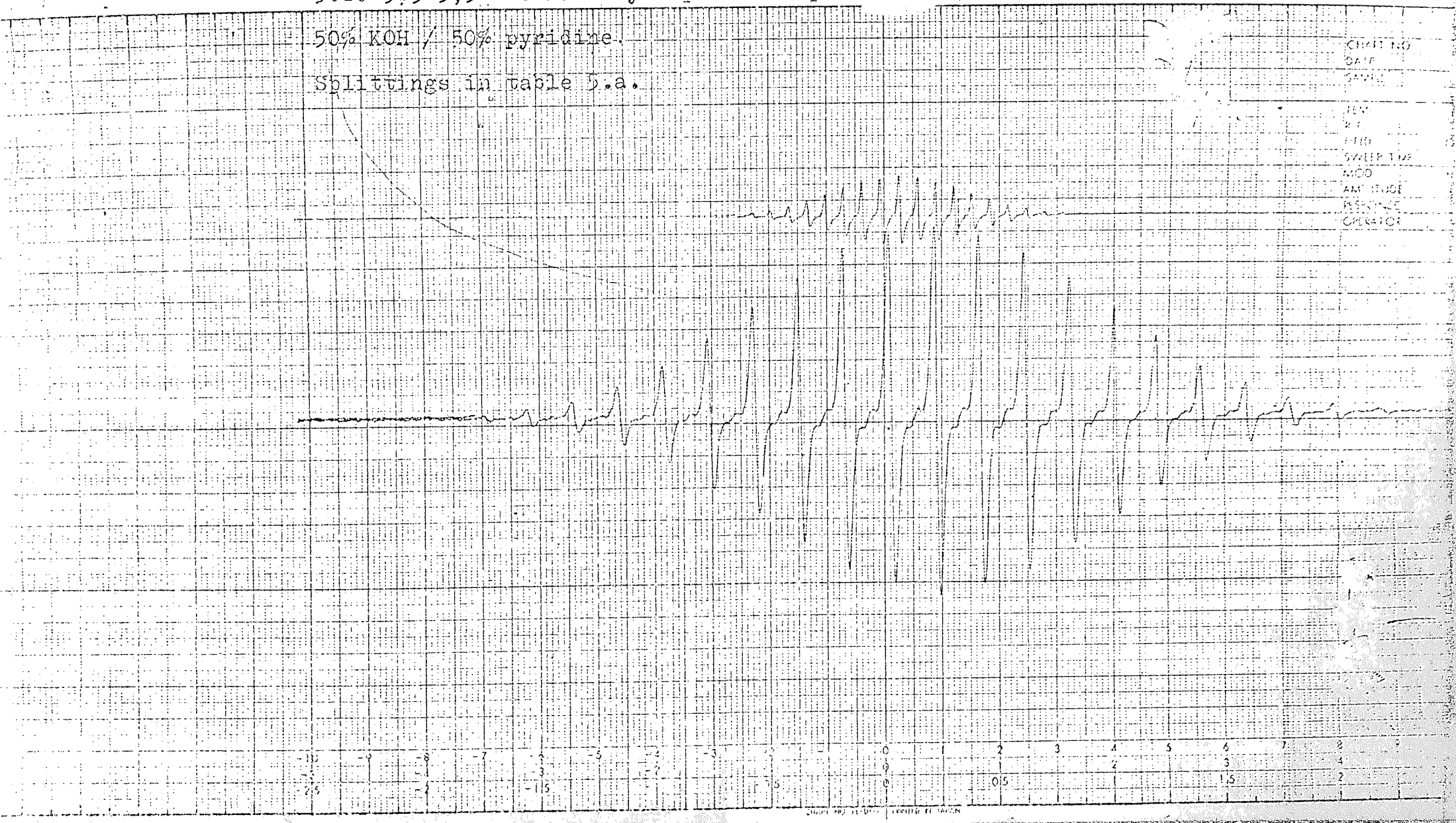
Splittings as in table 5.a.



5.2. 3,3'5,5'-Tetramethyldiphenosemiquinone anion.

50% KOH / 50% pyridine.

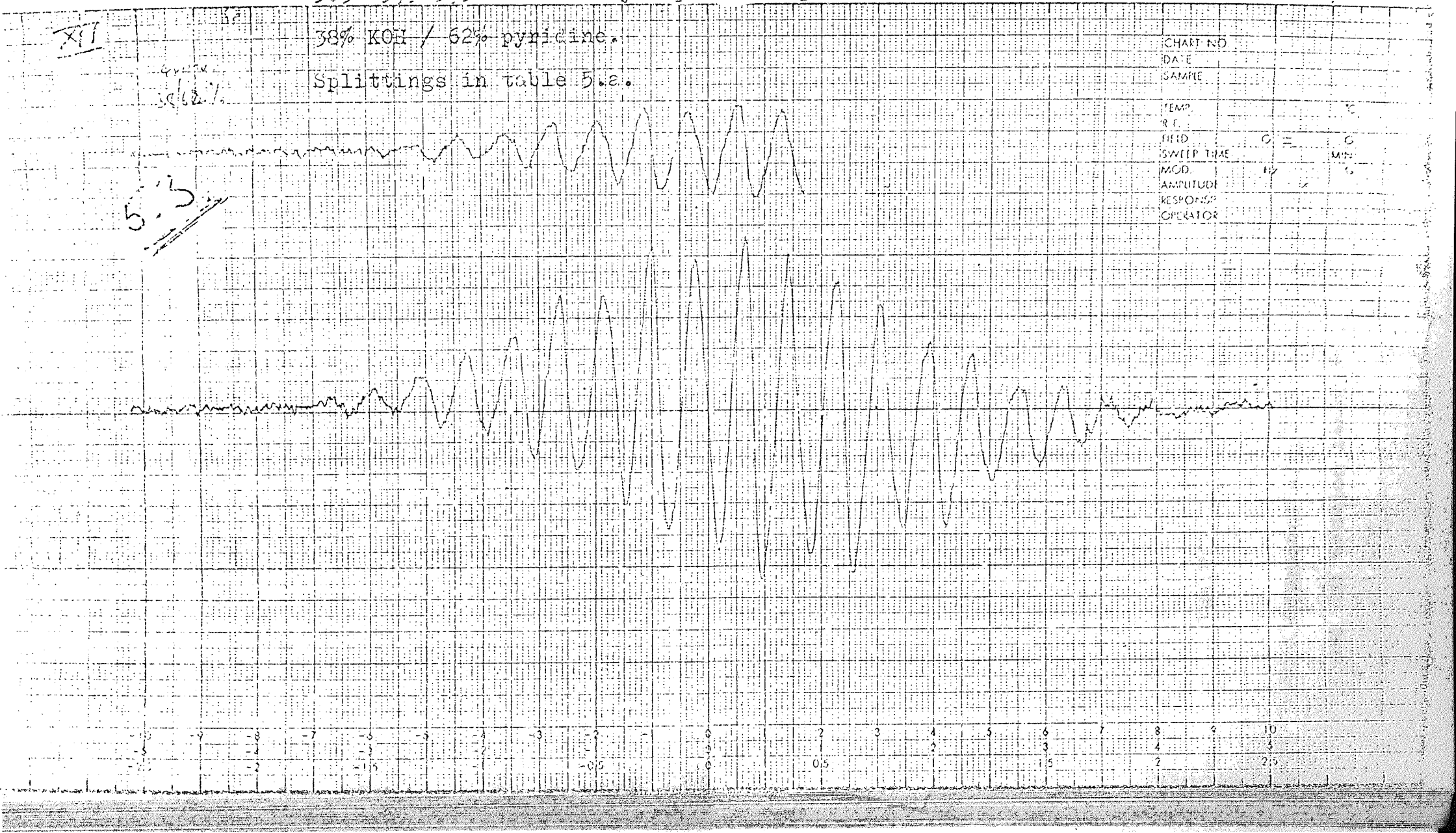
Splittings in table 5.a.



5.3. 3,3'5,5'-Tetramethyldiphenosemiquinone anion.

38% KOH / 62% pyridine.

Splittings in table 5.a.



showing the difference in resolving power between the two spectrometers used during the course of this research.

2. The 3,3',5,5'-tetramethoxydiphenosemiquinone anion.

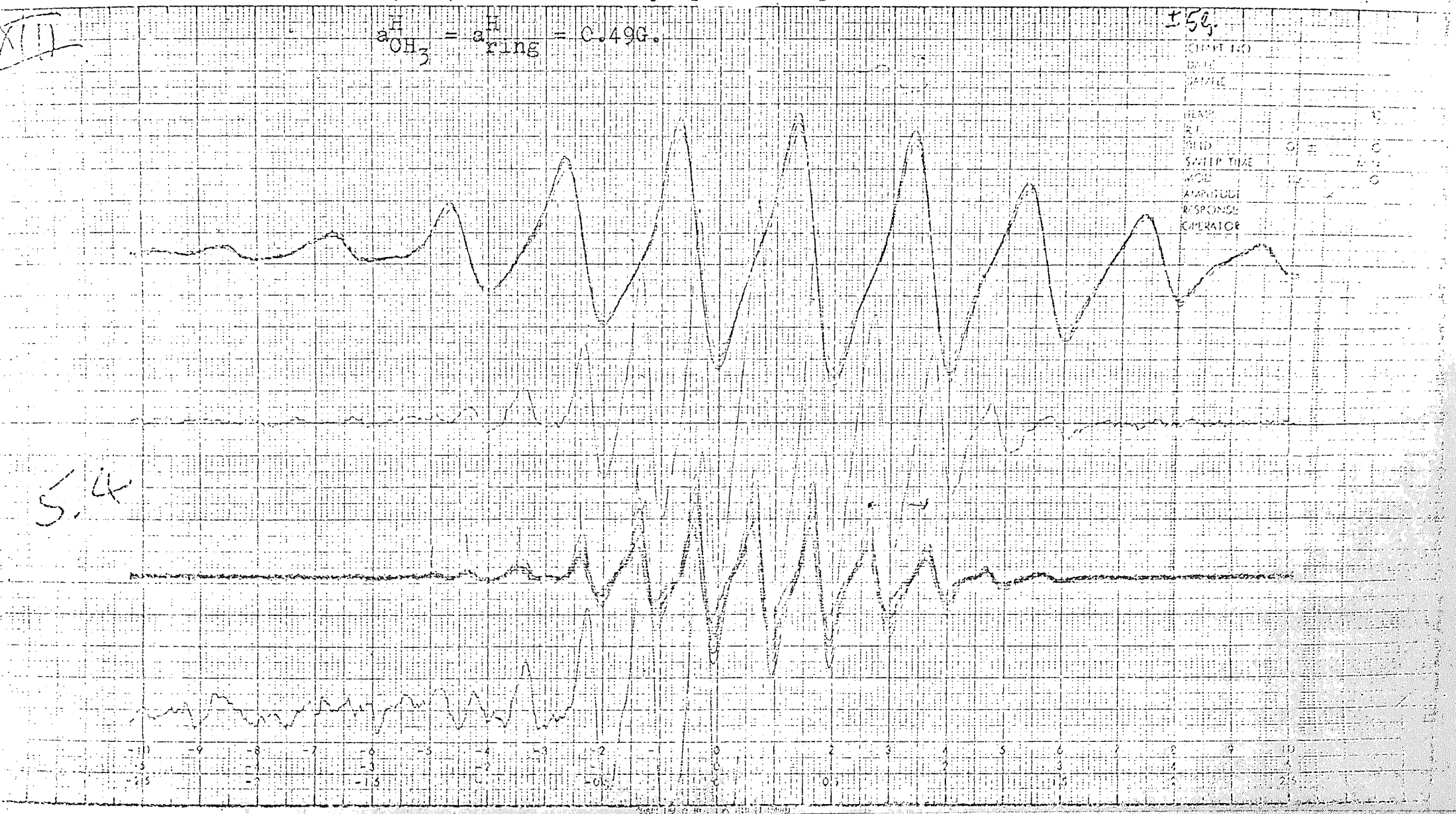
This species was produced by the general method of partial reduction of the parent quinone, and gave e.s.r.spectrum 5.4. The spectrum consists of thirteen equally spaced lines with a splitting of 0.5G, which is comparable to the earlier values (31,34), showing the splittings of both ring and methylgroup protons to be the same. Spectrum 5.4. was recorded in a solvent mixture of 50% KOH : 50% pyridine but when the solvent composition was altered, no variation in the values of the splitting constants was observed.

3. The 3,3',5,5'tetra-sec-butyldiphenosemiquinone anion.

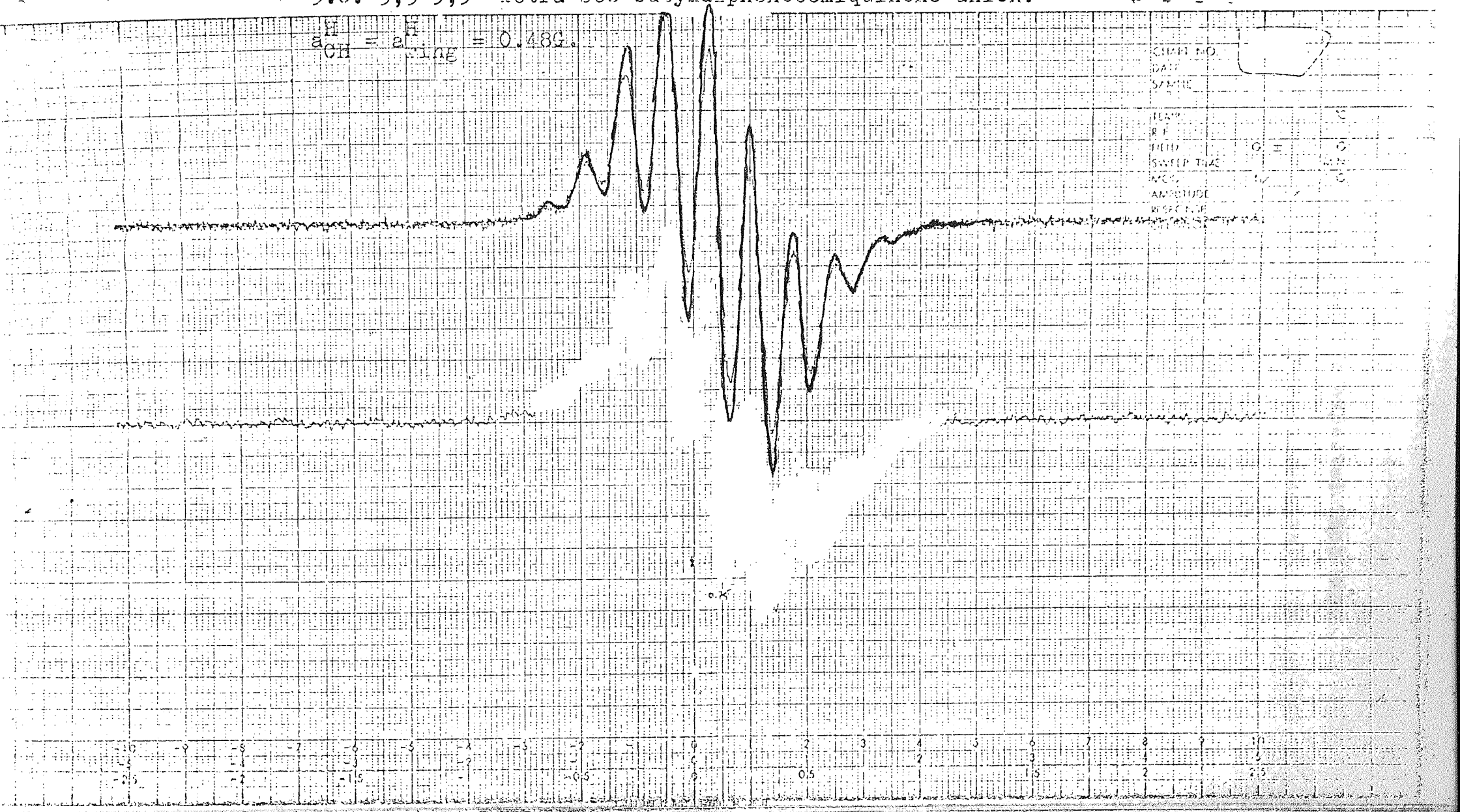
Previous studies (34) of this radical in a solvent mixture of KOH / pyridine, but produced by the air oxidation of the corresponding diol, have given a simple five line spectrum with a splitting constant of 0.48G, arising from the interaction of the four equivalent protons at positions 2,2',6 and 6'. However, when produced by the partial reduction of the parent quinone, the e.s.r.spectrum consists of nine equidistant lines, spectrum 5.6. These nine lines are due to the interaction of eight equivalent protons, thus there must be a similar degree of interaction from the ring protons and the methin protons of the sec-butyl groups. The cation radical of this species also shows a nine line spectrum. A study of this radical in solvents of varying

5.4. 3,3'5,5'-Tetramethoxydiphenosemiquinone anion

$a^H_{OCH_3} = a^H_{ring} = 0.496.$



5.6. 3,3'5,5'-Tetra-sec-butyldiphenosemiquinone anion.



composition was not made but it is expected that this radical does exhibit the effect (see discussion).

4. The 3,3',5,5'-tetraisopropyldiphenosemiquinone anion.

This radical, again produced by the general method described earlier, give a nineteen line e.s.r.spectrum, 5.7. This spectrum is due to the interaction of two groups of four equivalent protons. The major value of the two splitting constants, 1.05G, is attributed to th methin protons in each of the isopropyl groups, while the minor value, 0.65G is due to the interaction of the ring protons.

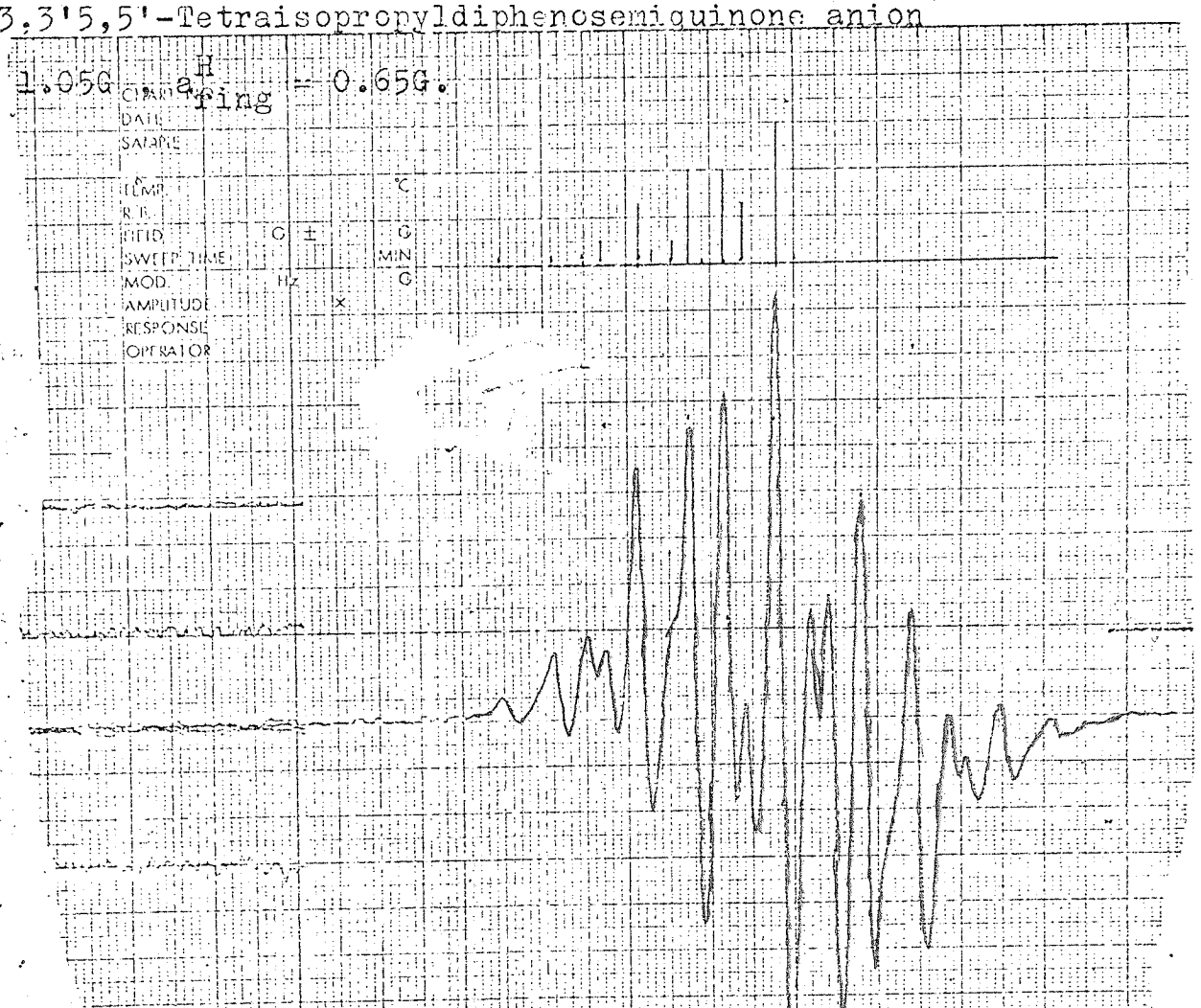
The hyperfine splitting constants obtained here compare favourably with those obtained for the radical when produced by air oxidation of the diol, and a similar solvent effect occurs.

5. The 3,3'-dimethyldiphenosemiquinone anion.

This radical has been previously reported (38), but has only been prepared by electrochemical methods. The e.s.r. spectrum was analysed in temrs of the interaction of four non-equivalent groups of protons, and the values of the splitting constants reported are shown in figure 5.b.

5.7. 3,3'5,5'-Tetraisopropyldiphenosemiquinone anion

a^{H}_{CH} = 1.05G, a^{H}_{ring} = 0.65G.



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5.8. 3,3'-Dimethyldiphenosemiquinone anion.

$a^{H}_{CH_3}$ = 1.68G , a^{H}_{ring} = 0.56G.

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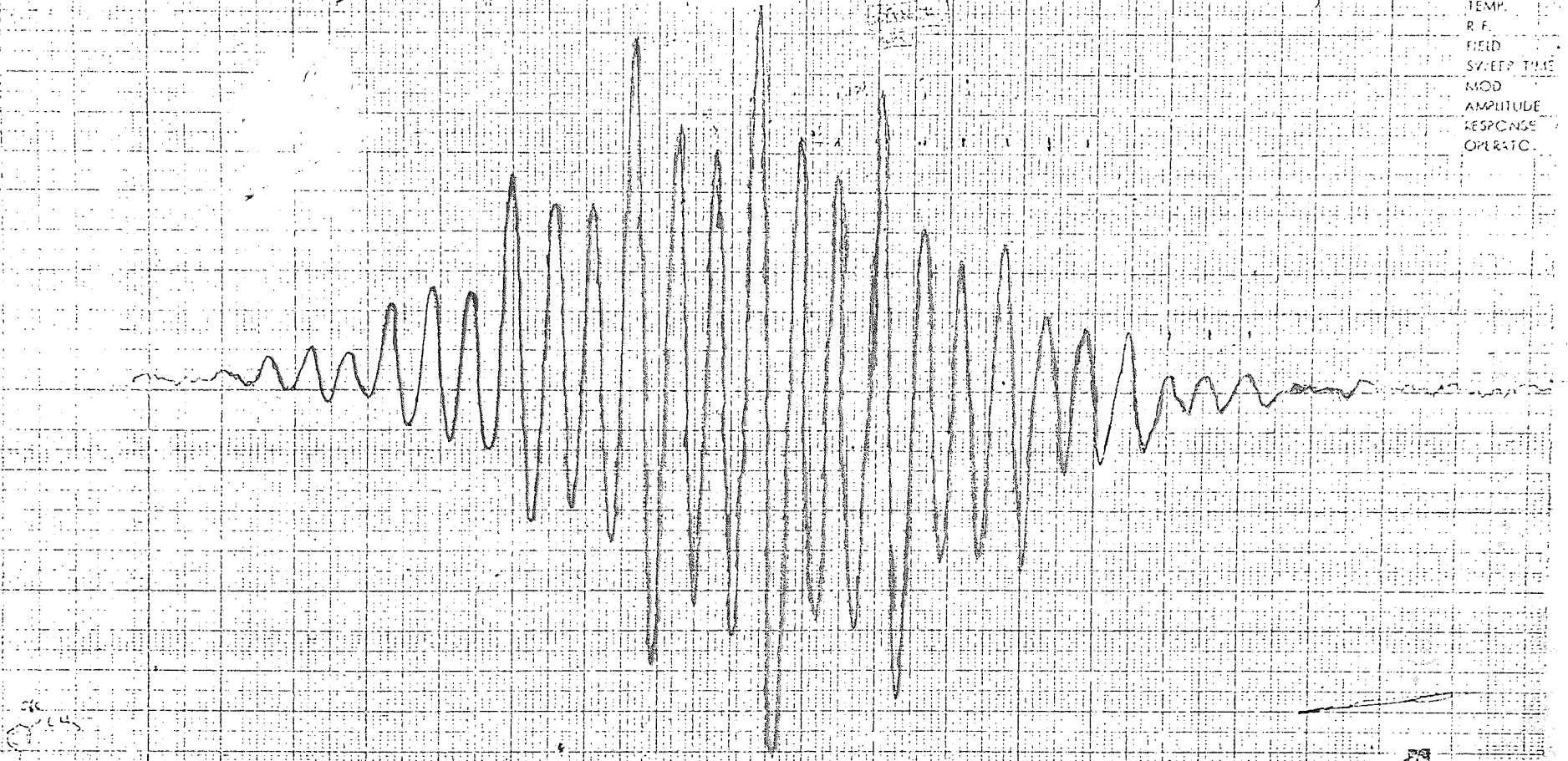
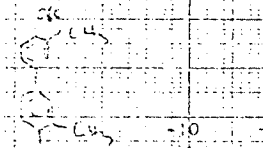
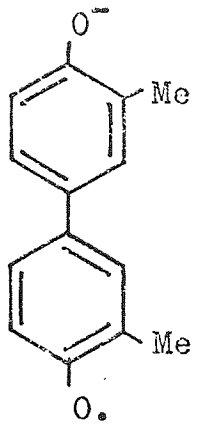
TEMP.
R.F.
FIELD
SWEEP TIME
MOD
AMPLITUDE
RESPONSE
OPERATOR







$a^{H}_{5,5'} = 2.36G,$
$a^{H}_{Me} = 1.96G,$
$a^{H}_{6,6'} = 0.78G,$
$a^{H}_{2,2'} = 0.48G.$ (38).

5.b.

When prepared by the air oxidation of 3,3'-dimethylbiphenyl-4,4'-diol, the radical gives an e.s.r.spectrum consisting of twenty five equally spaced lines as in spectrum 5.8. The spectrum is analysed in terms of two groups of six equivalent protons, having splitting constants of 1.68G and 0.56G. If we assume that the major splitting arises from the six methyl group protons, this means that the seemingly non-equivalent ring protons must be giving a similar interaction. This result is discussed later in the chapter.

Part IV : Discussion.

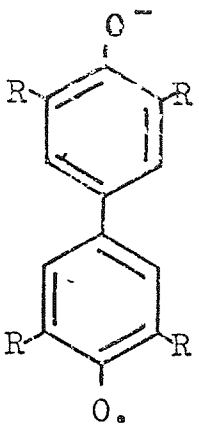
Previousto this work, diphenosemiquinone anion radicals have been produced chemically, solely by the air oxidation of the corresponding biphenyl-4,4'-diol. Although the method utilised here is different, this difference has little effect on the e.s.r.spectra of the species produced. Both chemical methods however, give appreciably different results to those obtained from similar species prepared by the electrochemical reduction of the parent quinone.

Comparing the two chemical methods, it is concluded that the method used here has several advantages over that used before. In general, the parent quinones of the tetraalkyldiphenosemiquinone anions are prepared by the oxidative coupling of the correspondingly substituted 2,6-dialkylphenol. Previously, the quinone so produced was then reduced using zinc dust and hydrochloric acid, to yield the biphenyl-4,4'-diol, which was then oxidised in the solvent mixture described earlier to give the anion radical. The reduction is time consuming and inefficient, so being able to produce the required radical species without this elaborate reduction process is obviously advantageous. The only exceptions are where the parent compound is produced by some other method which yields the biphenyl-4,4'-diol directly, e.g. in this work 3,3'dimethylbiphenyl-4,4'-diol is synthesised directly from 3,3'-dimethylbenzidine by a Sandmeyer reaction (see chapter 2,part A, 4.), and the diphenosemiquinone radicals are produced from this product.

The theoretical predictions of Matsunaga (32) regarding the magnitude of the hyperfine splittings due to the ring and methyl group protons in the 3,3',5,5'-tetramethyldiphenosemiquinone anion have been conclusively proved by the observation here of all the theoretically possible twenty nine lines in the e.s.rspectrum. The twenty nine lines arise from the interaction of a group of twelve equivalent protons (a = 1.78G) with a group of four equivalent protons (a = 0.56G).

Earlier studies involving the 3,3',5,5'-tetra-sec-butyldiphenosemiquinone anion, reported the e.s.r.spectrum of the radical to consist of five equally spaced lines with a splitting constant of 0.48G, but no spectrum was submitted in that work (33). The nine line spectrum shown here (5.6.) clearly shows the interaction of eight equivalent protons and this means that there are similar contributions from the methin protons of the sec-butyl groups and the ring protons, the value of the splitting constant being 0.75G.

If a comparison is made between the splitting constants of alkyl group protons of thetetraalkyldiphenosemiquinone anions as in figure 5.c., it may be seen that the magnitude of the alkyl proton splitting decreases from R = Me to R = ^{s}Bu, while the value for the ring protons remains similar.



R = Me, a^H_{Me} = 1.56G, a^H_{ring} = 0.76G,

R = ^{i}Pr, a^H_{CH} = 1.05G, a^H_{ring} = 0.71G,

R = ^{s}Bu, a^H_{CH} = 0.75G, a^H_{ring} = 0.75G,

R = ^{t}Bu, a^H_{Me} = -. , a^H_{ring} = 0.68G.

5.c.

It is known that in the radicals where R = methyl and R = isopropyl, they exhibit a marked solvent effect when produced in protic/aprotic solvent mixtures (33). The solvent-ion effect theory of Gendell (81) has been applied to these examples. It is postulated (33) that, within the solvent cage, quinone--aprotic solvent complexes are formed. Three possible complexes are shown in figure 5.d

i), $S_p---(Q^-)---S_p \rightleftharpoons S_p + (Q^-)---S_p$

ii), $(Q^-)---S_p \rightleftharpoons S_p---(Q^-)$

iii), $S_p---(Q^-) \rightleftharpoons (Q^-) + S_p$

5.d.

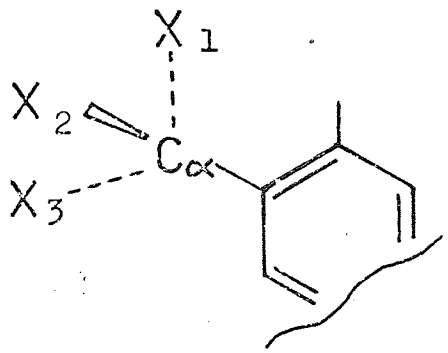
where Q^- represents the semiquinone anion and S_p a molecule of aprotic solvant.

Although no quantitative agreement can be found for either the doubly or singly hydrogen bonded solvent molecule cases (i and iii), correlation with experiment was found for ii. Although the species Q^----S_p is asymmetric, there

must be an equal number of S_p---Q^- species, so providing the rate of exchange is fast, any non-equivalence of the interacting protons giving the e.s.r.spectrum is averaged out.

Although no quantitative measurements were made in this work on the R = ^{s}Bu anion radical, it appears that a solvent effect does occur in the KOH /pyridine solvent mixture used here, and some general observations may be made as a result.

If, in the general case, the carbon atom of the alkyl substituent that is bonded to the quinone ring at position 3 is termed the α-carbon atom, it may be noted that in all cases where solvent interaction occurs in alkylated diphenosemiquinone anions, the alkyl proton splittings arise from the proton or protons attached to the α-carbon atom (see 5.e.)



i), R = Me, X_1= X_2= X_3= H.
ii), R = ^{i}Pr, X_1= X_3= Me, X_2= H.
iii), R = ^{s}Bu, X_1= Me, X_2= H, X_3= Et.
iv), R = ^{t}Bu, X_1= X_2= X_3= Me.

5.e.

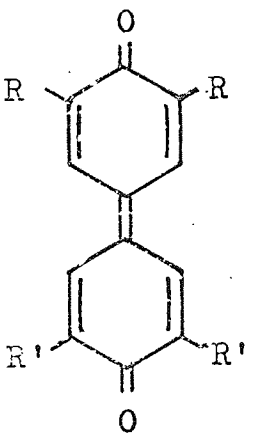
Where R = Me, the mechanism producing the hyperfine interaction is one of hyperconjugation (see chap.4.IV.2.) while where R = ^{i}Pr, and R = ^{s}Bu, the splitting is produced by a direct coupling of the methin proton in each, through the C_3- C bond. When R = ^{t}Bu no alkyl proton splitting

is observed and thus no solvent interaction can occur, firstly because of the asymmetry of the methyl group protons with respect to the molecular plane of the quinone rings, and secondly because even though there is an appreciable spin density on the α-carbon atom, the methyl protons are too far from the centre of the conjugated radical to show any direct coupling through the $C_3 - C_\alpha - C_\beta$ bond system, as there can be little spin density on the β-carbon atom.

It may be concluded therefore, that in such examples where an alkyl substituent has a proton or protons attached to the α-carbon atom, the hyperfine splittings are expected to vary with solvent composition and thus show a solvent ion effect as described by previous workers (81,33). This is because the protons attached to the α-carbon atom are in direct contact with the solvent cage and the Q^-----S_p complex, so any change in solvent composition must affect not only the interaction of these protons but also the free-electron spin density on the α-carbon atom. As, in these examples, pyridine (generally an electron donating aprotic solvent) is added, it increases and stabilises the spin density on the α-carbon, as a result the alkyl proton interaction increases (with this increase in spin density on the α-carbon) and thus the hyperfin splitting constant will increase. Likewise the splitting is expected to decrease as the proportion of protic solvent is increased. Both these predictions are borne out experimentally.

In the past, one or other of the two previously known diphenosemiquinone anions exhibiting solvent-ion interaction have been studied individually, in a number of aprotic / protic solvent mixtures (the aprotic solvent being pyridine 2-picoline, diethylamine etc.)and only the effect applied to the tetramethyldiphenosemiquinone anion has been examined extensively. Further studies involving the tetraisopropyl and tetra-sec-butyl anions would enable a general view as to the role and effect of each solvent to be formulated, and thus a general understanding of the solvent-ion effect theory in semiquinone anions, to experimentally verify theoretical predictions may result.

Particularly relevant to this work, future courses of research besides those already outlined might include the study of mixed alkyl substituted diphenoquinones as in figure 5.f.



$R \neq R'$

5.f.

The only previously prepared cross-coupled phenol is 3,5-dimethyl-3',5'-dimethoxydiphenoquinone, where R = Me and R' = OMe, which was produced by cross-coupling the two corresponding 2,6-disubstituted phenols with DDQ,

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (83). Further diphenoquinones where R' = ^{i}Pr or ^{s}Bu might furnish intersting e.s.r.results, and also where R = ^{i}Pr and R' = ^{s}Bu would enable a comparison of the coupling constants of the methin protons in either group.

The 3,3'-dimethyldiphenosemiquinone anion radical, produced by the air oxidation of the corresponding diol yields e.s.r. spectrum 5.8. This spectrum as described earlier is clearly defined and unambiguous, and all twenty five lines are of sufficient intensity to suggest that any further lines in each wing of the spectrum would be clearly seen, there being little baseline noise. There have been only three reported examples of diphenosemiquinone anion radicals exhibiting ring proton splitting from the positons 3,3'5 and 5' protons (38,84). The radicals in these examples have been produced electrochemically, and the hyperfine splittings of these protons have been of the order of 2.3G. However, if this were true for this case, the spectral extent for 5.8.should theoretically be of the order of 19.4G, while in actual fact it is quite unambiguously 13.6G, with little to suggest that the splittings involved could compensate for the difference of 6G. The spectrum 5.8 is consistently reproducible. The analysis given here that the ring the ring protons give an equivalent interaction (a = 0.56G) is the only way of accounting for the observed spectrum. If the ring protons were not equivalent, a more complex spectrum, arising from four different splitting constants would result (see fig.5.b). The differences between the splittings found here and those of Petranek (38) and Gerson (83) are difficult

to account for, but precise theoretical molecular orbital calculations should make clear any anomaly.

As a footnote, it is interesting to note that when Matsunaga dicovered the 3,3',5,5'-tetramethyldiphenosemiquinone anion (31), his initial analysis and assignments of hyperfine splitting were wrong(the ring proton splitting being of the order of 2.36G) but were later corrected after Huckel molecular orbital calculations had been made, with the ring proton splitting corrected to 0.54G, and this result has been conclusively proven in this chapter by the observation of all the spectral lines theoretically possible for the first time.

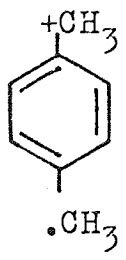
CHAPTER SIX.

DIPHENOSEMIQUINONE CATION RADICALS.

Part I : Previous Studies of Semiquinone Cations.

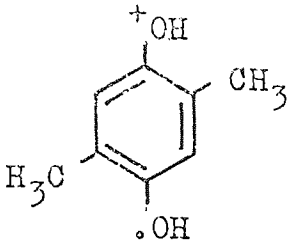
The first radical cation species to be produced for examination by e.s.r.spectroscopy were the cations of aromatic hydrocarbons (napthalene, anthracene, phenanthrene perilene etc), these were produced in solution by the oxidation of the parent compound in concentrated sulphuric acid (85,86,87,).

While studying the oxidation of 1,4-dimethylbenzene by potassium persulphate in concentrated sulphuric acid, Bolton and Carrington (88) noted that the methyl proton coupling constant of 3.89G in the e.s.r.spectrum, attributed to cation I,



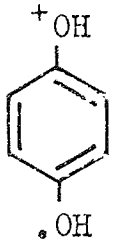
I

was much lower than the predicted value of 6G (89). In a subsequent paper (26), the spectrum was reassigned to cation II, the 2,5-dimethyl-1,4-benzosemiquinone cation.



II

The coupling constant of the hydroxyl protons is nearly identical to that of the ring protons. This conclusion was supported by a subsequent experiment in which methoxybenzene, phenol and 1,4-dihydroxybenzene wereeach oxidised by potassium persulphate in concentrated sulphuric acid, and 1,4-benzoquinone was reduced by sodium dithionite in the same medium. All four solutions gave identical e.s.r.spectra, consisting of five lines, arising from four equivalent protons, each split into triplets. The spectrum was assigned to the 1,4-benzosemiquinone cation (III).



III.

Furthermore, spectra identical to that arising from the persulphate oxidation of 1,4-dimethylbenzene were obtained firstly, by the reduction by sodium dithionite of 2,5-dimethyl-1,4-benzoquinone and secondly, by the oxidation of 2,5-dimethyl-1,4-dihydroxybenzene, both reactions taking

place in concentrated sulphuric acid.

Cation radicals of 2,5-dihydroxy-1,4-benzosemiquinone, 1,4-napthosemiquinone and 9,10-anthrasemiquinone were studied by Bolton, Carrington and Santos Viega (90). The first two were prepared by the dithionite reduction of the parent quinone, while 9,10-anthraquinone could only be reduced using zinc dust and hydrochloric acid. The e.s.r.spectrum of 9,10-anthrasemiquinone was found to consist of twenty one broad, ill resolved lines, while in dideuterated sulphuric acid a well defined spectrum was produced. Analysis showed that only hydroxyl protons had exchanged for deuterons in this latter case, and therefore the lack of resolution in the former spectrum was attributed to the rapid exchange of the hydroxyl protons in sulphuric acid.

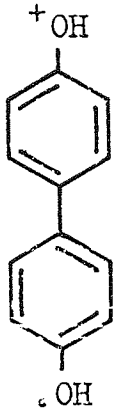
Later work (91,92,93) on the tetramethyl-1,4-benzosemiquinone, 1,4,5,8-tetrahydroxynapthalene and 1,4-dimethoxybenzene cations, provided evidence for slow rotation effects and rotational isomers about the C - O bond (see chap.4), and in some cases the barriers to rotation were calculated. Depending on whether this rotation was at fast, intermediate or slow rates, the alternating linewidth effect could be observed.

While attempting to prepare positive ions of aromatic molecules, Buck, Bloemhoff and Oosterhoff found that organic nitro- compounds in combination with acids or Lewis acids, possess good electron attracting properties (94). As a result, Forbes and Sullivan (34) found that a mixture of aluminium chloride and nitromethane was readily effective in preparing cation radicals by oxidation. Often, the concentration of radicals was greatly enhanced using this method of production, e.g. the concentration of cation radicals of 1,4-dimethoxy-benzene in sulphuric acid is about 1%, while in the mixture of aluminium chloride and nitromethane the concentration of radicals approximates to 100%. The viscosity of the solvent mixture is lessthan that of sulphuric acid and thus, the high-field line broadening often observed in the latter medium is decreased, owing to a smaller contribution to the linewidth from anisotropic dipolar interactions. Furthermore some reactions may be studied over a greater temperature range owing to the lower melting point of the system.

It was observed that in some cases, oxidation by the solvent mixture of aluminium chloride / nitromethane goes beyond the one electron stage (34). Studies on the oxidation of biphenyl -4,4'-diol showed that on mixing a blue paramagnetic solution attributed to the diphenosemiquinone cation was obtained but, on the addition of excess aluminium chloride, a yeloow dia-magnetic solid was formed (the process being reversible with the addition of more nitromethane).

Part II. : Previous Studies of Diphenoquinone Cations.

The oxidation of biphenyl-4,4'-diol by hydrogen peroxide or potassium persulphate in 98% concentrated sulphuric acid has been reported by Wheway (33). When the diol is added to sulphuric acid containing a trace of oxidant, a blue solution is obtained , the e.s.r.spectrum of which shows seventeen equally spaced lines and is assigned to the diphenosemiquinone cation VI.



$a^{H}_{2,6}$= 2.05G
$a^{H}_{3,5}$= 0.71G.
(see spectrum 4.1.)

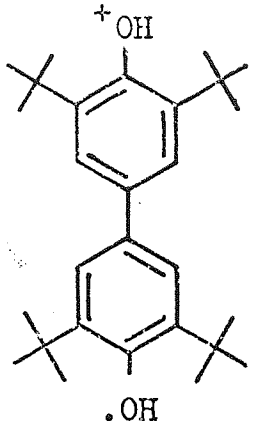
VI

A similar spectrum is obtained by the reduction , by sodium dithionite, of diphenoquinone, in the same medium. The absence of hydroxyl proton splitting is accounted for by the fact that the rate of exchange of the hydroxyl protons is fast compared with the e.s.r.transition time.

When larger amounts of substrate are used, sulphonation reactions occur, the products being precipitated in the solution, and being identifiable using n.m.r. and ultraviolet absorption spectroscopy.

3,3',5,5'-Tetra-tert-butyldiphenoquinone was found to yield a paramagnetic solution when dissolved in concentrated

sulphuric acid (33). The resulting e.s.r.spectrum was analysed as being due to the interaction of one group of four equivalent protons with a gourp of two equivalent protons, and was considered to arise from cation VII.



VII

Paramagnetic solutions were also obtained from the similar tetraisopropyl and tetra-sec-butyl compounds but in both cases the spectra consisted of a single broad unresolved line.

The alkylated diphenoquinones were also studied in a solvent mixture of aluminium chloride and nitromethane but the results were inconcusive although a great deal of hyperfine splitting was observed in the spectra produced. These complex spectra were thought to arise from secondary radicals produced while dealkylation reactions were occurring and thus definitive analysis of the spectra was precluded.

Part III : Present Work.

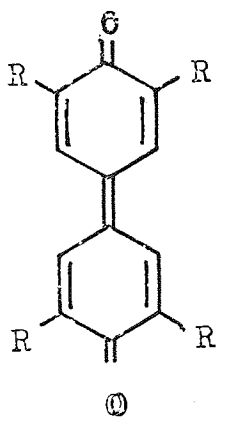
A re-examination, with a view to continuation and extension of the reactions of the tetra-alkylated diphenoquinones in concentrated sulphuric and 98%dideuterated sulphuric acids, was undertaken, noting any deviation of the results and observations from those obtained previously.

The deuteration of diphenoquinone in dideuterated sulphuric acid was examined in order to extend the previous work (33) to a conclusive result, but this proved largely unsuccessful without the variable temperature equipment required to carry out such a study.

Part IV : Results.

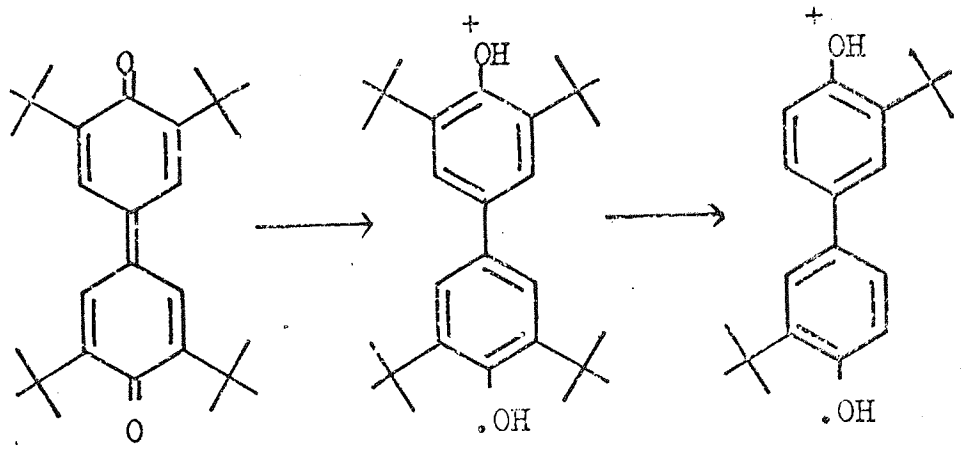
3,3',5,5'-Tetraalkyldiphenosemiquinone Cations.

Compounds of type VIII were synthesised (chap.2) and the e.s.r.spectra produced by dissolving a little of either in $2cm^3$ of concentrated sulphuric acid, to which a trace of hydrogen peroxide had been added, were recorded .



VIII

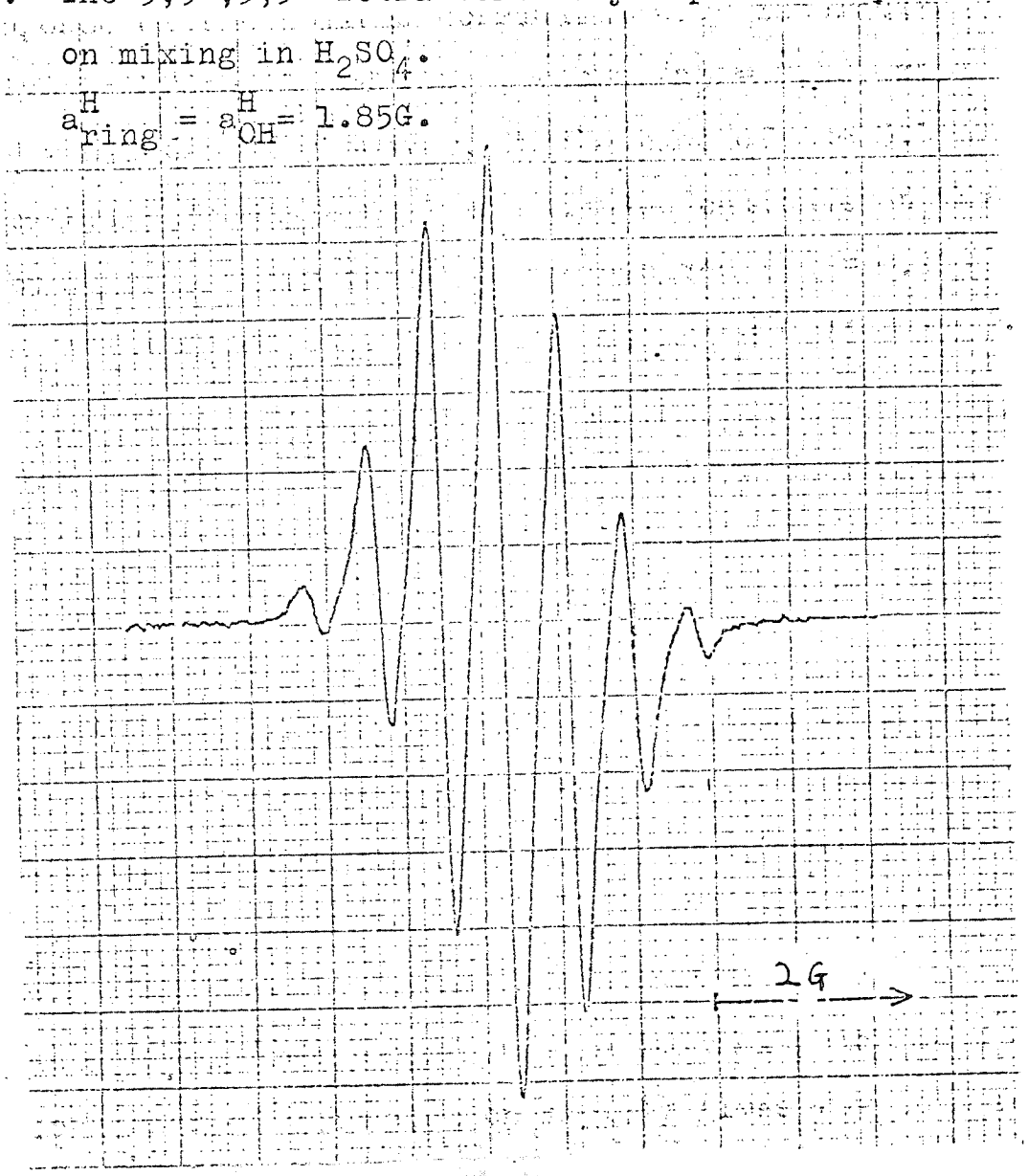
On mixing, the tetra-tert-butyl compound, when dissolved in sulphuric acid, consistantly gave a seven line e.s.r.spectrum as in 6.1. When the spectrum is recorded again after five minutes spectrum 6.2 results. A spectrum such as 6.1 results from the interaction of six equivalent protons (a = 1.85G), and this is further split by a group of two equivalent protons to give 6.2, the value of the splitting constant being 1.49G. It is believed that in 6.1 the seven line spectrum is produced by there being an equivalent interaction of the ring and hydroxyl protons and then a dealkylation takes place in either ring, with the alkyl group being replaced by another proton in each case, and these two ring protons give the further splitting. The complete reaction is shown below.



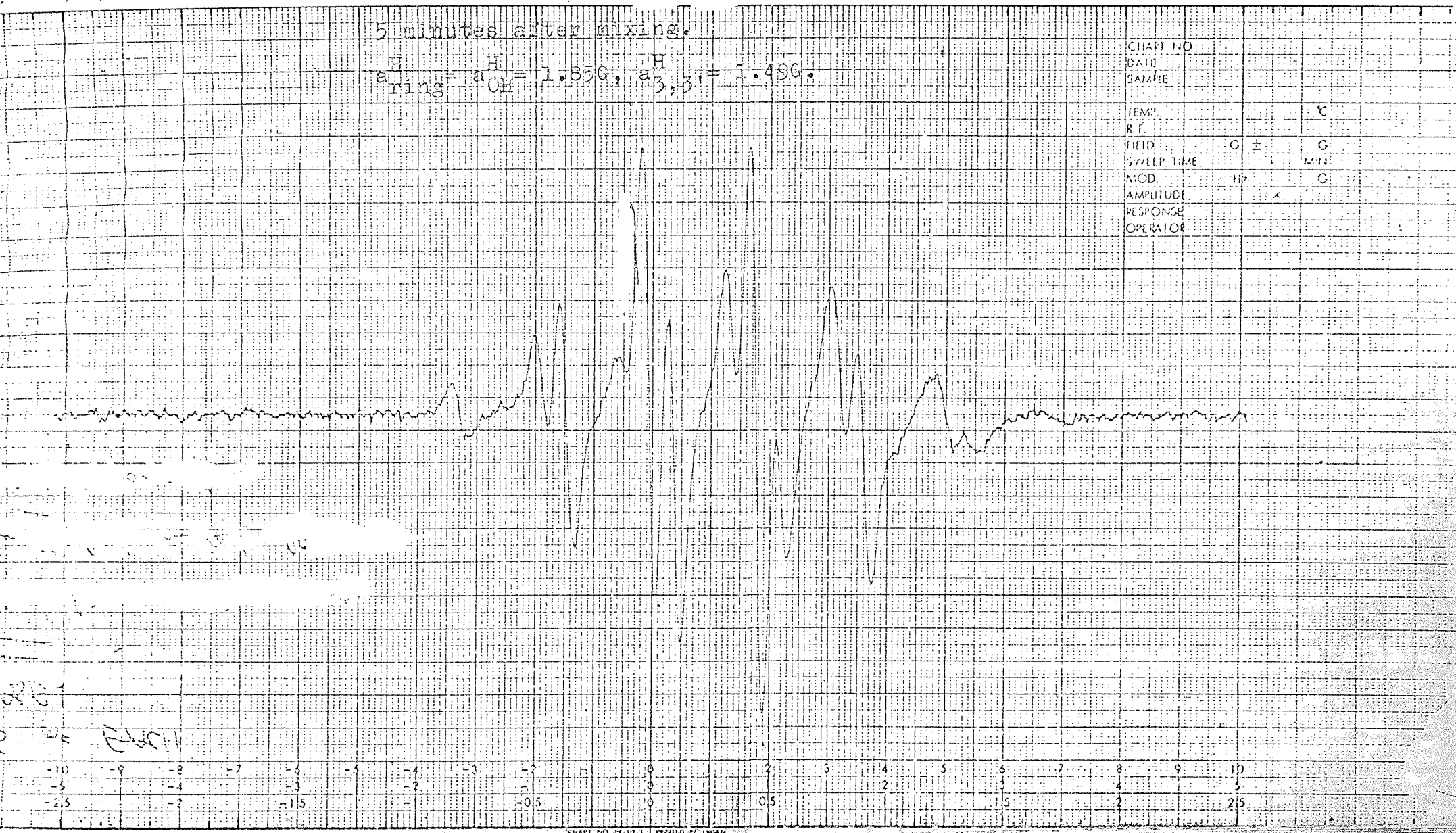
The previous examination of the tetra-sec-butyl analogue showed that the e.s.r.spectrum produced from the cation consisted of a single broad line. However in this work the spectrum was closely re-examined and although difficult to resolve fully, the spectrum, 6.3, showed a degree of hyper-fine splitting. It appears that there are nine shoulders on

6.1. The 3,3',5,5'-Tetra-tert-butyldiphenosemiquinone cation on mixing in H_2SO_4.

$a^H_{ring} = a^H_{OH} = 1.85G.$

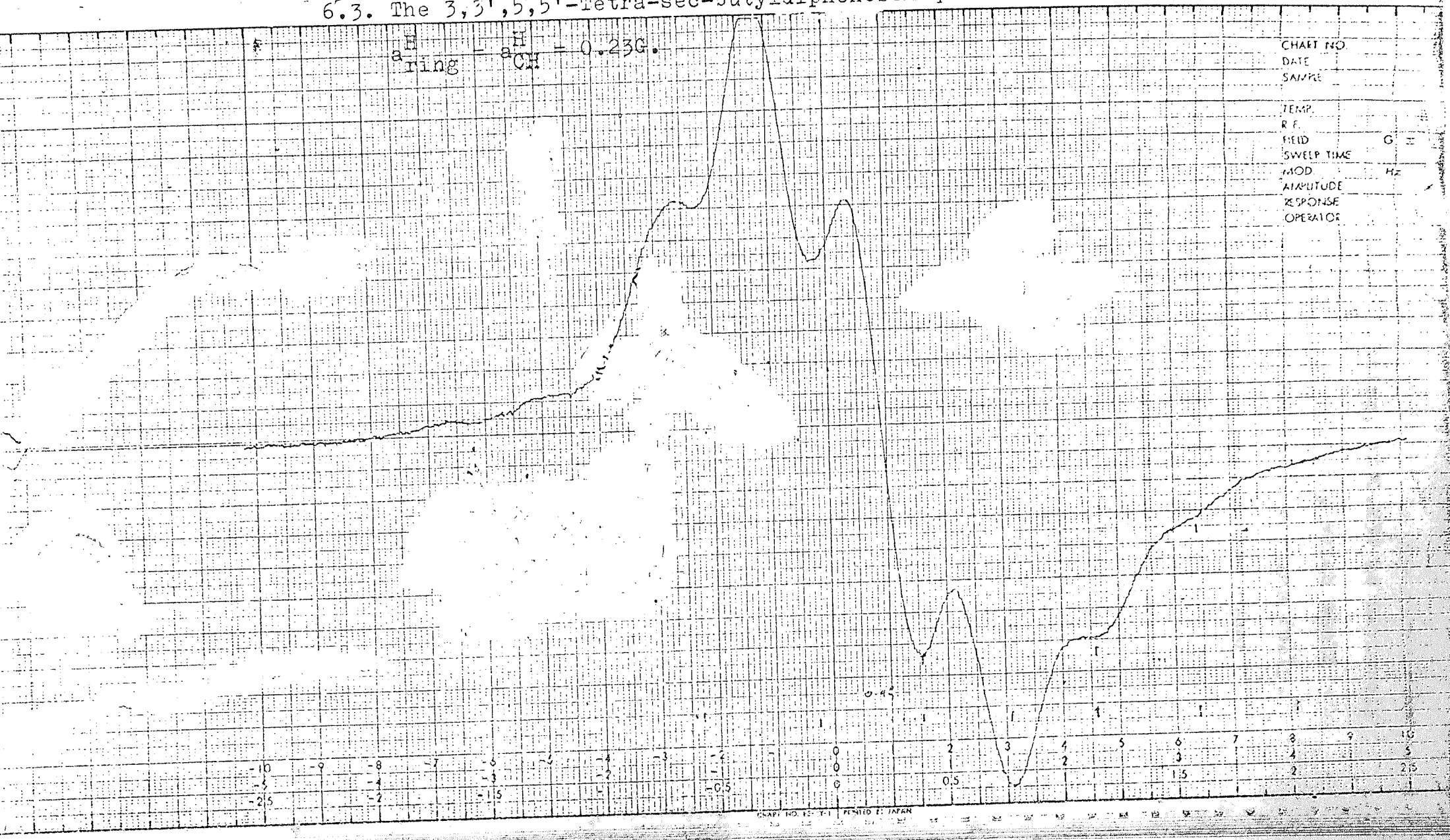


6.2. The 3,3',5,5'-Tetra-tert-butyldiphenosemiquinone cation.



6.3. The 3,3',5,5'-Tetra-sec-butyldiphenosemiquinone cation.

$a^{H}_{ring} - a^{H}_{CH} = 0.23G.$



the broad resonance and the splitting, of 0.23G is obviously approaching the minimum linewidth detectable, which would account for the inability to resolve the nine lines fully. Although the splittings are much smaller than any other yet observed from a diphenosemiquinone cation, it appears that the nine lines would come from the interaction of the four ring protons with the four methin protons of the sec-butyl groups.

When the tetramethyldiphenoquinone was examined under similar conditions to the other compounds, a paramagnetic solution could only be produced when sodium dithionite was present, a result consistent with that obtained previously.

Part V : Discussion.

When studying the behaviour of 3,3',5,5'-tetra-tert-butyl diphenoquinone in a solvent mixture of aluminium chloride and nitromethane, Wheway (33) noted that initially a seven line spectrum was produced, the splittings being similar to those obtained here. After ten minutes, the spectrum became more complex, with a great deal of hyperfine splitting as, presumably dealkylation reactions took place. The initial seven line spectrum was attributed to the interactions of the ring and hydroxyl protons (the contributions being equivalent). In sulphuric acid however, only the spectrum similar to 6.2 was obtained, it is thought that in this earlier work, the time lapse between mixing, deoxygenation and recording the spectrum was long enough for the dealkylation reaction shown above to be completed and thus the initial

seven line spectrum would not be observed. Here, the primary study was made without deoxygenating the solution, with the result that the initial semiquinone cation was observed prior to dealkylation. No splitting was observed from the alkyl group protons in this example.

Also, if the earlier interpretation is correct, and there is a significant non-equivalent interaction from the hydroxyl protons with the ring protons, assuming that rotation of the hydroxyl group might be severly restricted by the tert-butyl substituents, a marked alternating linewidth effect would be apparent. In this analysis, no such effect would be observed due to the fact that the interactions of both sets of protons are the same, so that after the initial seven line spectrum has disappeared, the secondary splitting must come from the protons where the de-alkylations have occurred.

CHAPTER SEVEN.

CONCLUSIONS.

Attempts have been made to characterise the addition and substitution chemistry of diphenoquinone and its related compounds. Attempts to produce cyano- substituted and mixed halo-/cyano- substituted diphenoquinones that may have high oxidation potentials failed. The reactions of diphenoquinone and 3,3',5,5'-tetramethyldiphenoquinone with amino-type compounds were studied and although in general, unsuccessful, products were isolated from the reactions between a), methylamine and tetramethyldiphenoquinone and b), ethylenediamine and diphenoquinone, these products could not be isolated and purified.

Products could not be isolated from the Thiele acetylation of unsubstituted diphenoquinone, but where the incoming acetyl-groups were specifically directed, acetlyation was efficient and readily affected. Acetylations were performed on a series of 3,3',5,5'-tetraalkyldiphenoquinones and in each case the corresponding 2,4,4'trihydroxybiphenyl was isolated.

Addition reactions of diphenoquinones are thought to proceed via a 1,8-addition, an example of which is reported here. The reaction, an acetylation of unsubstituted diphenoquinone with acetyl chloride yields two products, biphenyl-4,4'-diol and 3-chlorobiphenyl-4,4'-diol.

A study of diphenosemiquinone free radicals by e.s.r. spectroscopy showed that some of the spectra observed exhibited an alternating linewidth effect. The intramolecular processes producing these effects were characterised using the e.s.r.results. The alternating linewidth effect was present in spectra arising from both diphenosemiquinone anions and cations.

In the 4,4'-dimethoxy- and 4,4'-diethoxybiphenyl cation radicals, the rotation of the alkyl groups about the C_4 - O bond is restricted sterically, as a result the e.s.r.spectrum arising from the eight protons in the diphenoquinone nucleus consists of four different values of splitting constant, from the interaction of the four non-equivalent pairs of equivalent protons. In the diphenosemiquinone cation, there is no interaction of the hydroxyl group protons, and the e.s.r.spectrum consists of seventeen equally spaced lines arising from the interaction of two non-equivalent groups of four equivalent protons.

No free radical cation can be detected when 4,4'-diphenoxybiphenyl is added to concentrated sulphuric acid containing a trace of oxidising agent,but when the phenyl groups have a p-nitro- substituent, dearylation takes place in this medium and the diphenosemiquinone cation is observed (the other product of the reaction being either nitrobenzene or nitrobenzene-4-sulphonic acid).

Diphenosemiquinone anion radicals are prepared by the oxidation of tetraalkylbiphenyl-2,4,4'-triols in a solvent mixture

of 2M potassium hydroxide and pyridine. The tetramethyl-compound initially gives a spectrum arising from the interaction of twelve equivalent protons giving the major splitting constant. This changes to a spectrum arising from the interaction of a group of six equivalent protons and a group of two equivalent protons, this spectrum shows and alternating linewidth effect which arisies from a combination of slow rotation about the 1 - 1' bond, and the rate of exchange of the two resonance forms of the radical. The spectra of the tetramethoxy and tetra-tert-butyl compounds each consist of a pair of triplets, from the interaction of the position 6 proton with the pair of equivalent protons at positions 2' and 6'. The first step in all these reactions is thought to be the production of a diphenosemiquinone anion, the deprotonation of the position 2 hydroxyl group being the overall rate determining step. The rate of deprotonation is fast in the tert-butyl case, but the methyl- and methoxy compounds show a slow deprotonation each producing initially complex e.s.r.spectra.

The oxidation of 2,2'4,4'-tetrahydroxybiphenyl in the same solvent mixture yields a dianion diradical, the e.s.r.spectrum of which shows a quartet of doublets from the interaction of three single non-equivalent protons, there being one free electron in each half of the molecule and no interaction by either across the 1 - 1' bond, which may be fixed due to the electrostatic repulsion of the negative charges residing on the oxygen atoms at positions 2 and 2'

Diphenosemiquinone anions were produced from the tetra-alkyl compounds by affecting their reduction in a 2 M solution of potassium hydroxide, these radicals were stabilised by the addition of an organic solvent such as pyridine. The effect of adding pyridine to these solutions may be described qualitatively in terms of the solvent dependence of these radicals that has been previously r reported. The qualitative description of the solvent effect theory fits the experimental results reasonably.

The anion radical of 3,3'-dimethyldiphenosemiquinone is reported, this radical was previously unprepared by chemical methods and on comparison large discrepencies in the splitting constants obtained here and those observed when the radical is produced by electrochemical methods are apparent.

The cation radical of 3,3',5,5'-tetra-sec-butyldiphenosemi-quinone was observed and a degree of hyperfine splitting, though small,is reported.

The reaction of 3,3',5,5'tetra-tert-butyldiphenoquinone in concentrated sulphuric acid was reexamined. The initial e.s.r.spectrum was found to consist of seven equidistant lines arising from a group of six equivalent protons, the ring protons and the hydroxylprotons having an equivalent interaction. Dealkylation then occurs and each line of the spectrum is split into triplets, by the protons at positions 3,and 3' after dealkylation.

APPENDIX I

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